



International Cooperation

**Seminar on
EMISSIONS AND AIR QUALITY**

Thessaloniki, October 9, 1990

edited by
N. Moussiopoulus
G. Kaiser

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Seminar on
EMISSIONS AND AIR QUALITY

edited by
Prof. N. Moussiopoulos
Dr. G. Kaiser

Organizing Institution:
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German-Greek-Cooperation
in Scientific Research and Technological Development

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Foreword:

G. Kaiser, International Bureau, Research Center Jülich

Like many other countries, Greece is facing severe environmental problems. Therefore, in the framework of the German-Greek Co-operation in Scientific Research and Technological Development, the integrated project "Environmental Engineering" was made operational beginning of 1990.

The project "Environmental Engineering", which has the highest priority ranking in the co-operation programme, comprises in 1990 the following subprojects:

- o Distribution of Nutrient and Metal Pollutions in the Elefsis Bay
- o Dispersion of Atmospheric Pollutants
- o Forest Damage Monitoring
- o Ozone Concentrations in the Atmosphere
- o Emission Data
- o Modern Mapping and Cadastral Techniques, and
- o Hellenic Emission Data Bank.

In order to review the progress achieved in the area of Air Pollution and to mutually agree on further activities, the seminar "Emissions and Air Quality" was held at the Aristotele University of Thessaloniki on October, 9, 1990.

The presentations given by the lecturers and the results of follow-up discussions with other participating experts clearly indicated that the subprojects on Air Pollution are progressing very well. For the additional working areas of the integrated project "Environmental Engineering" major achievements can be stated, too. Therefore, the financial support given by the Federal Ministry for Research and Technology (BMFT) and the General Secretariat for Research and Technology in the Ministry of Industry, Energy and Technology (GSRT) to the institutions involved, is well justified.

P R O G R A M M E

EMISSIONS AND AIR QUALITY

Seminar in the Framework of the Scientific Co-operation
between the Federal Republic of Germany and Greece

Thessaloniki, October 9, 1990

P R O G R A M M E

- 9:30: Dr. G. Kaiser, Research Center Jülich, International
Bureau
Overview on the German-Greek Co-Operation Programme in
Scientific Research and Technological Development
- 9.50: Dr. Z. Samaras, Aristotle University Thessaloniki
Air Pollution from Road Traffic in Greater Athens;
Analysis and Perspectives
- 10.10: Dr. H. Güsten, Nuclear Research Center Karlsruhe
Photochemical Processes in the Atmosphere
- 10.30: Prof. N. Moussiopoulos, Aristotle University Thessaloniki
Modelling of Atmospheric Transport Phenomena in Athens
- 10:50: Dr. G. Heinrich, Nuclear Research Center Karlsruhe
Immission Measuring Techniques
- 11.10: Dr. N. Kyriakis, Aristotle University Thessaloniki
Laboratory Measurements of Automotive Exhaust Emissions
- 11.30: Dr. Ch. Holzapfel, Research Center Jülich
Estimation of Emission Data as Input for Long Range
Transport Calculations

L E C T U R E S

OVERVIEW
ON
THE GERMAN-GREEK CO-OPERATION PROGRAMME
IN
SCIENTIFIC RESEARCH AND TECHNOLOGICAL DEVELOPMENT

G. Kaiser
International Bureau, Research Center Juelich

1.) Introduction:

On November 11, 1978, the Minister for Research and Technology of the Federal Republic of Germany and the Minister for Co-Ordination of the Hellenic Republic signed an intergovernmental agreement on a co-operation in Science and Technology between the two countries.

Based on this legal framework, some hundreds of joint research projects have been successfully implemented over the years, resulting in remarkable scientific and technological achievements of mutual benefit.

2.) Outline of the Co-operation Programme:

The general objective of the bilateral co-operation is

"to pool the national resources in science and technology for the economical, ecological and industrial benefit of both countries".

The main activity to achieve this goal is the implementation of research projects jointly defined and executed by German and Greek scientists/engineers. Specifically, the implementation process may comprise:

- o the exchange of scientists,
- o the provision of special equipment items to the research teams,
- o the execution of workshops and seminars, and
- o other scientific and/or technological activities being in line with the specific objectives of a joint project.

The implementation of the projects is financially supported by the German Federal Ministry for Research and Technology (BMFT) and the Greek General Secretariat for Research and Technology in the Ministry of Industry, Energy and Technology (GSRT).

Responsible for the overall management and monitoring of the programme is on the German side the International Bureau of the Research Center Juelich and on the Greek side the General Secretariat for Research and Technology.

3.) Structure of the Co-operation Programme 1990

The co-operation programme 1990 comprises a total of 42 operational projects.

A break-down to working areas results in the following programme structure:

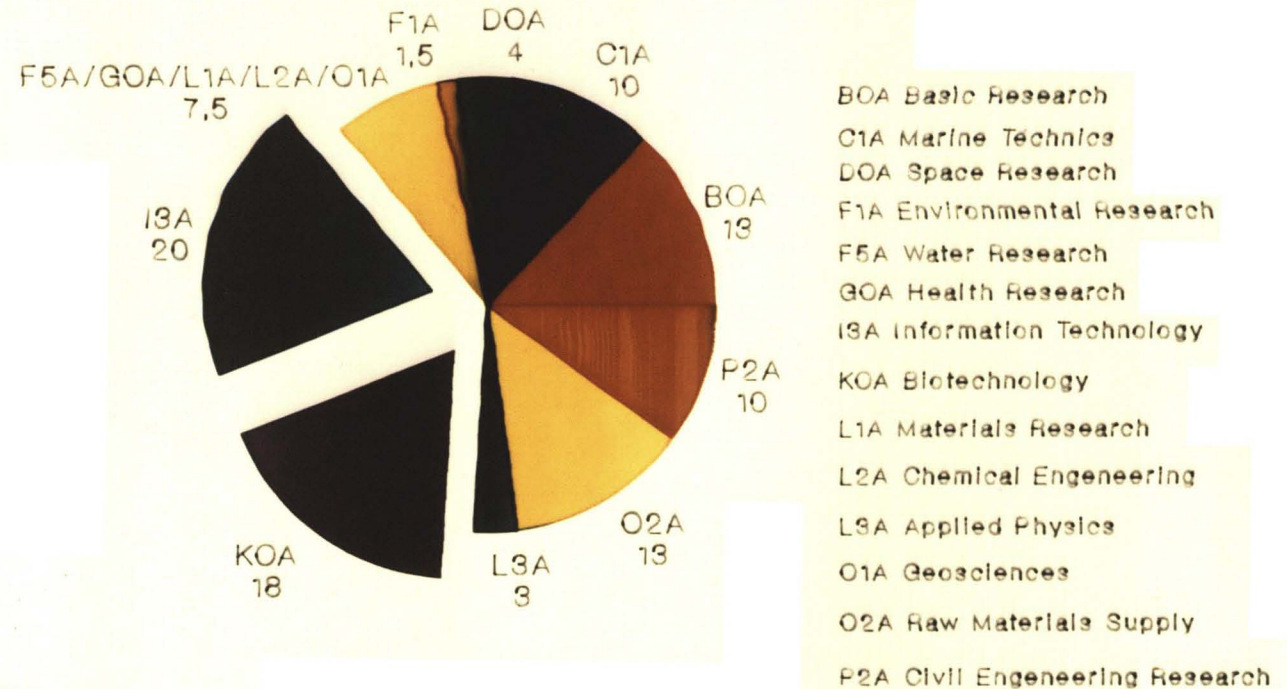
o Basic Research:	4 Projects
o Marine Research:	1 Project
o Space Research:	2 Projects
o Environmental Research:	7 Projects
o Water Research:	1 Project
o Information Technology:	5 Projects
o Biotechnology:	6 Projects
o Materials Research:	4 Projects
o Chemical Engineering:	2 Projects
o Applied Physics:	4 Projects
o Geosciences:	1 Project
o Raw Materials Supply:	3 Projects
o Civil Engineering Research:	2 Projects

4.) Distribution of FRG Funds by Working Areas:

The planned distribution of the FRG funds '90 by working areas is shown in Fig. 1.

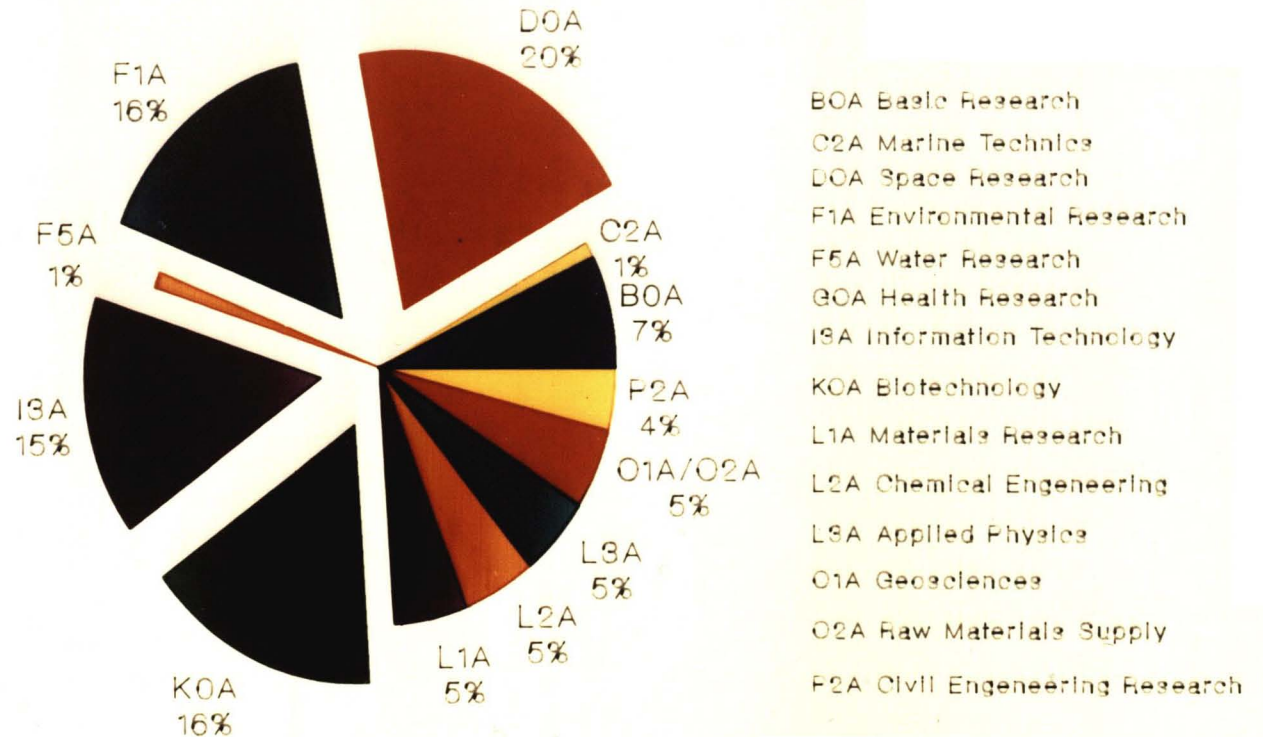
A comparison with the allocation of funds in 1989 (Fig. 2) reflects the programmatic changes performed in 1990. Whereas in the past for example basic research had been a major component of the programme, emphasis is now on projects with social impact, especially on environmental ones. The increase of the financial support for this working area from 1.5% to 16% clearly indicates the importance given by both sides to the identification and solution of problems relating to an improvement of the living conditions of the population of Greece.

Distribution of FRG Funds 1989 by Working Areas



KFA/GRE05

Distribution of FRG Funds 1990 by Working Areas



AIR POLLUTION FROM ROAD TRAFFIC IN GREATER ATHENS ANALYSIS AND PERSPECTIVES

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Abstract

A computer programme, FOREMOVE, whose development has been supported by the Commission of the European Communities, has already been used for the baseline estimation of future road traffic emissions for all Member States of the Commission.

The baseline run for Greater Athens has shown that an accelerated adoption of catalytic technology for new vehicles can only partially counterbalance the steeply increasing trends of traffic emissions (Figure 1 and Table I). It is expected that the total gaseous emissions (CO, VOC and NOx) from traffic by the year 2000 will be up to 50% higher than in 1985. These results led to the identification of the main parameters which influence the behaviour of the system:

- highly increasing motorization (Figures 2 and 3),
- longer life-times for cars (Figure 4)
- rather elevated annual mileages especially in urban areas

The validity of the above considerations was demonstrated using two different scenarios:

- market intervention, assuming a major change in the Greek car market from 1991 onwards, similar to that in Germany (Figure 5)
- mileage limitation, assuming a 50% reduction for in-city driving mileage (Figure 6)

Traffic emissions in 1970, i.e. before photochemical episodes were reported, were calculated and compared with those estimated for the future. This showed that cleaner cars, higher replacement rates for old vehicles and reductions for in-city mileage could form the basis of a policy decision for the reduction of traffic related pollution in Greater Athens.

More specifically such a policy should focus on:

- accelerated introduction of clean vehicles (closed loop 3-way catalysts & carbon canisters) to the Athenian fleet;
- retrofitting of catalysts & carbon canisters to in-fleet vehicles;
- transformation of the existing ring, currently limited to "random traffic restrictions", into a "ring with limitations for polluting cars", as an incentive to the introduction of the catalysts and reduction of in-city mileage;
- development of an "Exhaust Gas Control Card" system for testing and control of in-use cars;
- considerations for the usage of diesel-engined passenger cars

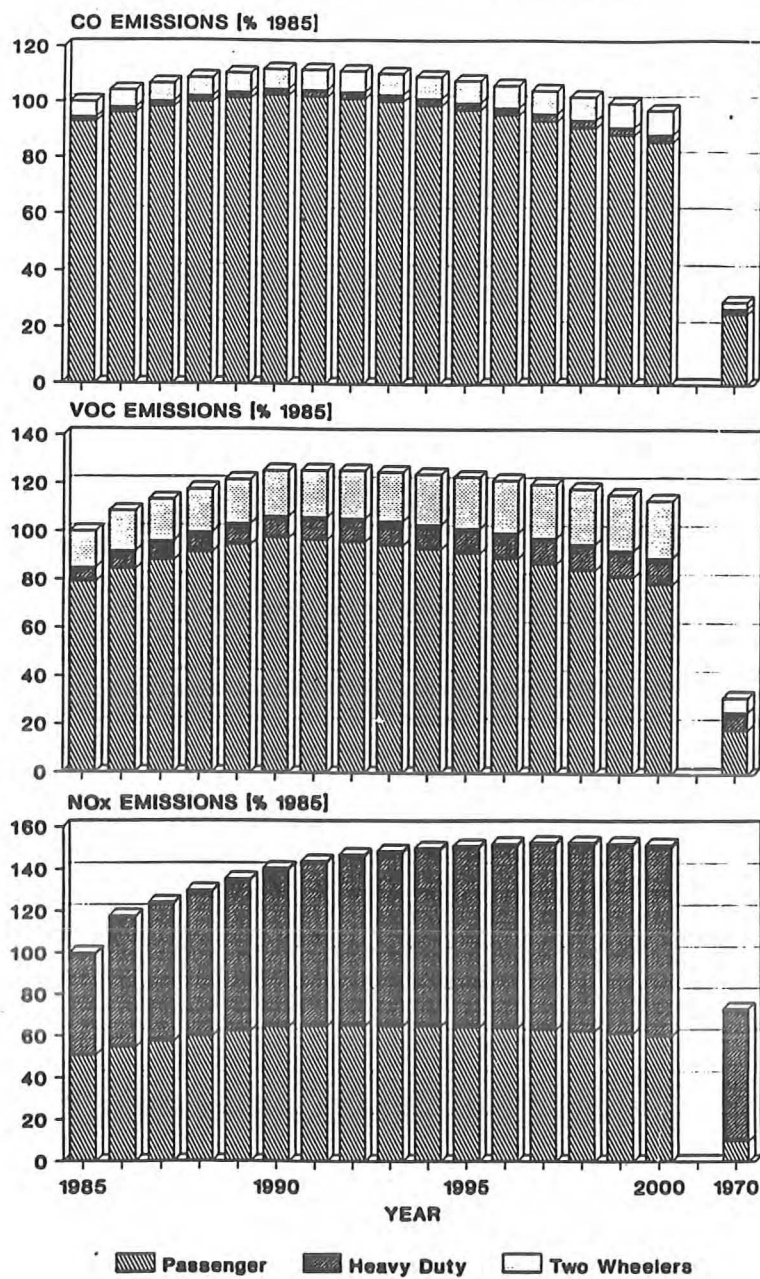


Figure 1: Estimation of future emissions in Greater Athens according to "Baseline Scenario"

Table I: Emissions to the atmosphere in Greater Athens. Reference Year 1990.

	VOC		NOx		CO		Smoke		Particulates		SO ₂	
	[kt]	[%]	[kt]	[%]	[kt]	[%]	[kt]	[%]	[kt]	[%]	[kt]	[%]
Road Traffic	81.1	(79)	27.8	(76)	538.2	(100)	3.3	(64)	0.1		1.4	(8)
Gasoline Veh.	75.2	(73)	14.9	(41)	526.8	(98)					0.2	(1)
Diesel Veh.	5.9	(6)	12.9	(35)	11.3	(2)					1.2	(7)
Industry	21.8	(21)	7.0	(20)	0.5		1.0	(20)	21.2	(100)	12.7	(71)
Central Heating	0.2		1.4	(4)	0.4		0.9	(16)			3.7	(21)
TOTAL	103.1	(100)	36.4	(100)	539.1	(100)	5.2	(100)	21.3	(100)	17.8	(100)

PASSENGER CARS IN ATHENS

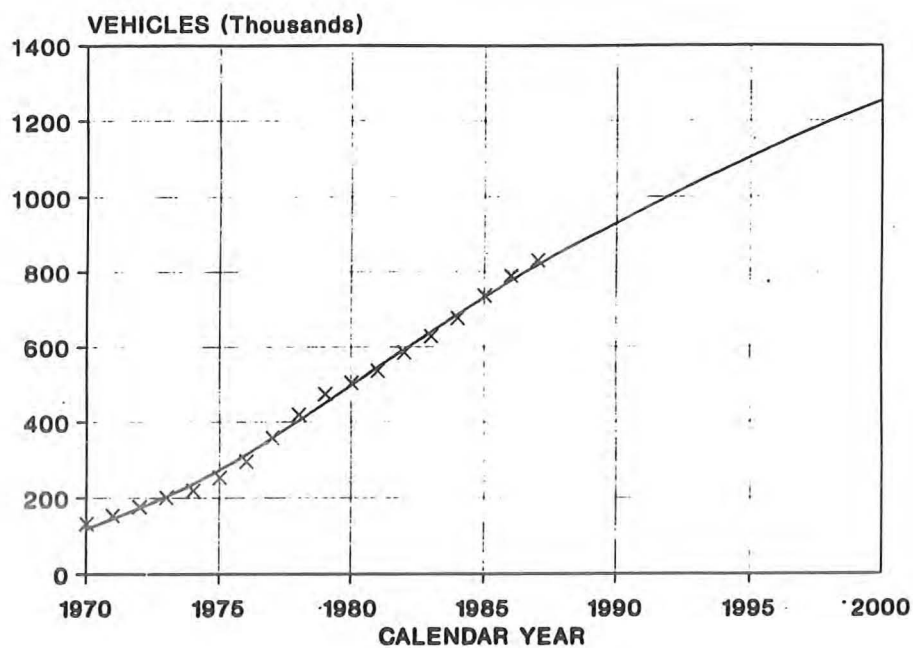


Figure 2: Estimation of the evolution of passenger car fleet in Greater Athens (X: Data, --: Prediction)

HEAVY DUTY VEHICLES IN ATHENS

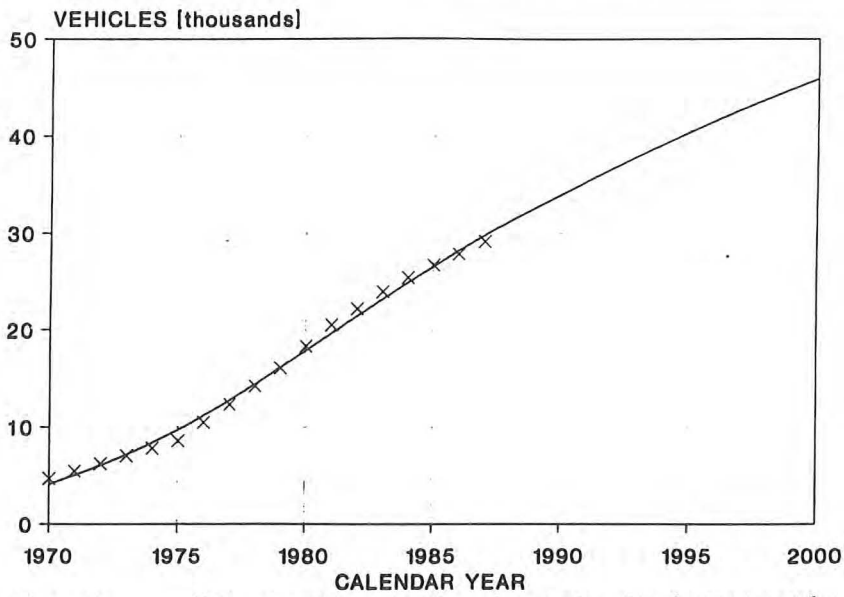


Figure 3: Estimation of the evolution of heavy-duty fleet in Greater Athens (X: Data, --: Prediction)

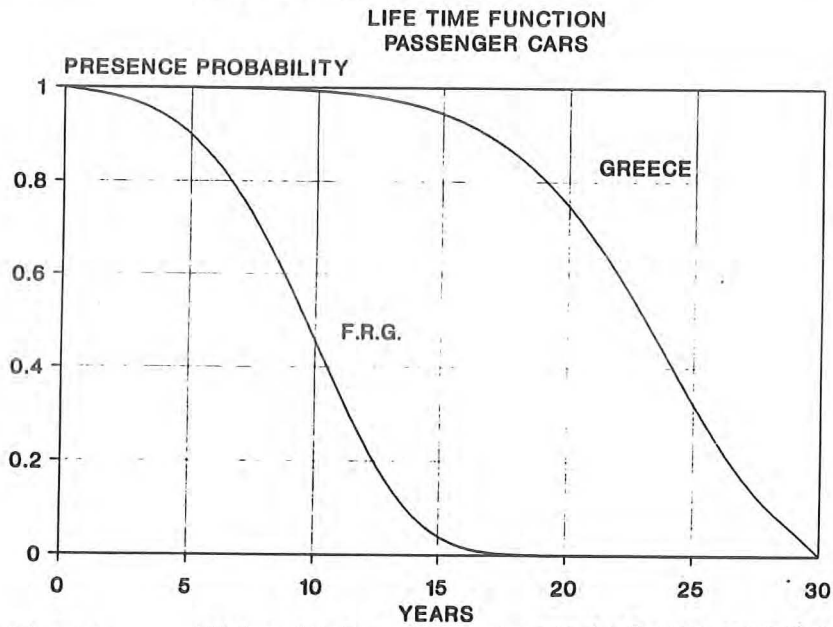


Figure 4: Lifetime function of passenger cars in Greece; comparison with Federal Republic of Germany.

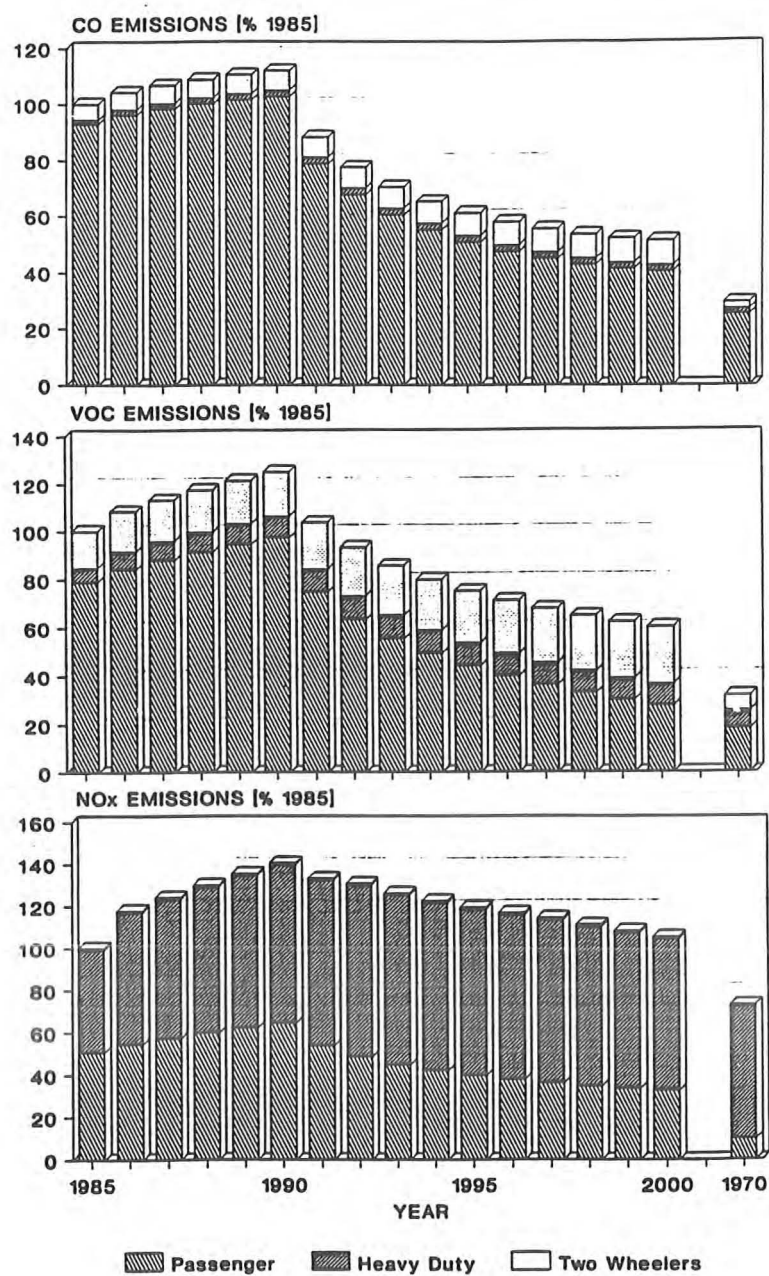


Figure 5: Estimation of future emissions in Greater Athens according to "Market Intervention Scenario"

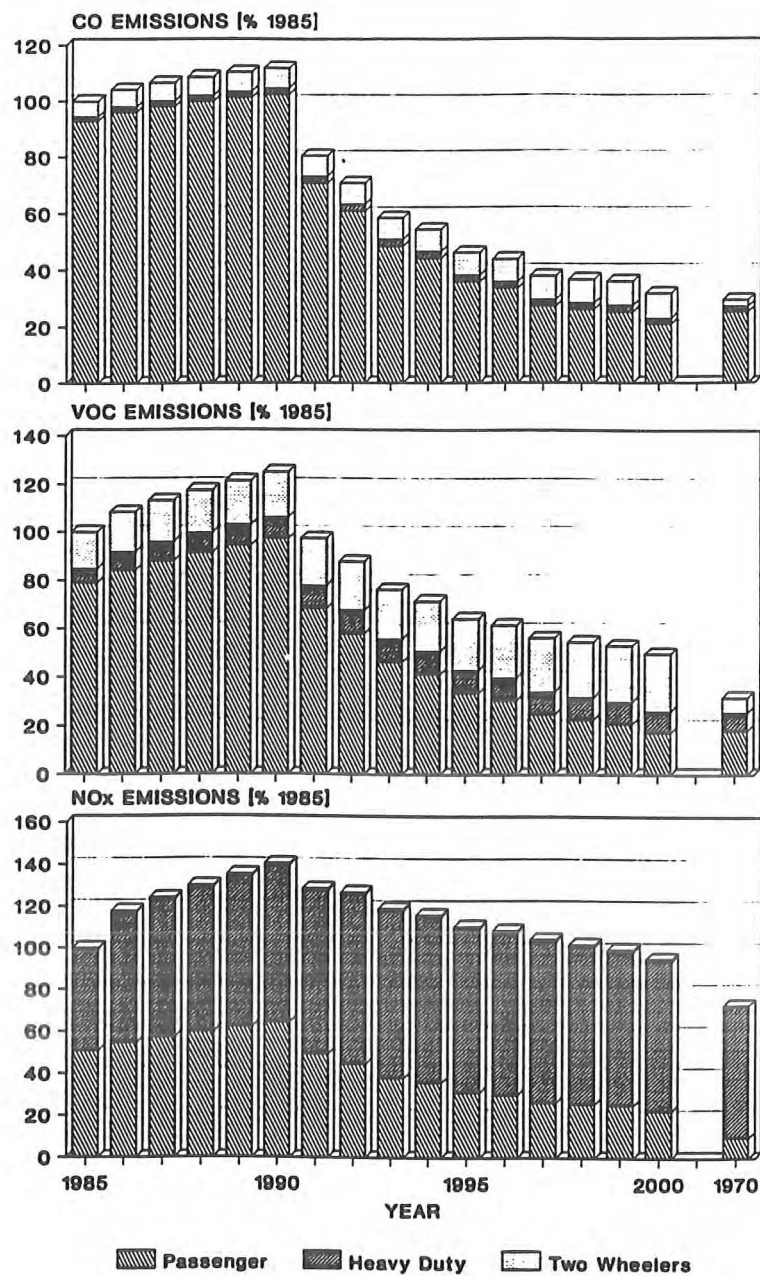


Figure 6: Estimation of future emissions in Greater Athens according to "Market Intervention and Mileage Limitation Scenario"

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Abstract

An introduction to the present knowledge of the chemistry of the reactions involved in photochemical air pollution is given with special emphasis on the situation in urban areas. For the area of Greater Athens an evaluation of the diurnal variation of the hourly ozone concentrations measured at five sites from June until early September 1984 within a German-Greek scientific cooperation programme revealed that photosmog episodes are always associated with the sea breeze circulation. Nearly all photochemical smog episodes with values exceeding for several hours per day the U.S. Air Quality Standard of 120 ppb ozone, were accompanied with well developed sea breezes. Due to local air circulation in the closed topography of the Greater Athens basin, precursors of ozone (NO_x and hydrocarbons) are transported to and accumulated over the Gulf of Saronikos during early morning hours while the land breeze is blowing from NE. Around noon, when the sea breeze from SW sets in, photochemically produced ozone formed over the sea is brought back to the coast and central Athens where it increases by a factor of 3 to 5 the local ozone concentrations within one or two hours.

Introduction

Photochemical smog is the result of photochemical reactions of dilute automobile exhaust with light in the wavelength range of 300-400 nm [Güsten, 1986]. The following events take place:

- Nitric oxide (NO) is converted to nitrogen dioxide (NO_2),
- when all of the NO has disappeared, ozone starts to appear,
- the hydrocarbons are oxidized and disappear,
- besides ozone, reaction products such as aldehydes and PAN (peroxyacetyl nitrate) are formed.

In general, photochemical smog is noticed by high concentrations of photo-oxidants above all ozone. These products above a certain concentration (120 ppb ozone) lead to

- eye irritation, coughs, chest discomfort, and fatigue,
- damage to vegetation, production loss in crops,
- damage to organic material (rubber, paint, organic tissue).

A general scheme for the formation of photochemical smog is depicted in Fig. 1. Beside rapid reactions of NO, NO₂ and ozone to an equilibrium, as indicated on the left side of the scheme, additional ozone is formed on the right side in complicated chain reactions of free radicals regenerating NO₂ from NO. In particular, the chain reactions are responsible for the rapid conversion of the unburned hydrocarbons to photo-oxidants within a few hours above an urban area. Thus, in a city like Athens, on sunny days at noon time several 100 tons of ozone have been formed from its precursors NO_x and hydrocarbons.

Photochemical Smog in Athens

Interesting phenomena of photochemical smog formation have been observed in coastal regions of metropolitan areas (Blumenthal et al., 1978; Bronstein and Thompson 1981; Lalas et al., 1983; Güsten et al., 1988). Athens, a city of more than 3.5 million inhabitants, is located in a small natural basin formed by mountain ranges on three sides and the Gulf of Saronikos to the southwest (Fig. 2). In this fairly small basin (≈ 450 km²) 50 % of all automobiles registered in Greece and 40 % of the Greek industry are concentrated. The high anthropogenic emissions in conjunction with the topographical and meteorological features result in high levels of photochemical air pollution, characterized by the appearance of a brown, hazy cloud over the city, called "Nephos" there. Oxidant levels in excess of the U.S. Air Quality Standard of 120 ppb ozone are built up frequently during the summer months (Cvitas et al., 1985; Güsten et al., 1988). In the next chapter we analyse the results of an ozone measurement campaign performed at various sites in Greater Athens from early June until early September 1984 (Güsten et al., 1988).

Results and Discussion

Figure 2 shows the map of Greater Athens with the monitoring sites (L, O, K, I and A). The residential areas are indicated by stippling and the 500 m height contours are traced. Winds blow mostly along the major NE-SW axis of the basin. Prevailing direction of the synoptic wind during the summer is NE. Hence, the air mass is advected from the basin to the Saronikos gulf. Strong insolation is the driving force for sea breeze flows, which develop during more than 30 % of the days in the

spring and summer months in the Athens area (Prezerakos, 1986). Sea breezes develop when solar radiation heats up the land surface more rapidly than the sea surface. The air begins to rise over the warm land and cooler air from the sea flows in to replace it (Fig. 3)

Analysing the diurnal ozone concentrations during the measurement campaign we have defined a photochemical smog episode when the ozone concentration in central Athens after noon time was higher than the U.S. Air Quality Standard of 120 ppb for more than two hours. The two measuring sites in downtown Athens were L on the Hill of Lykabetos and O, the National Observatory of Athens. While in June 1984 the ozone concentrations did not exceed 120 ppb, two smog episodes were observed in July 1984. The first on 10 and 11 July, started with an abrupt change in wind direction at noon when the north-northwesterly winds at $3\text{--}5\text{ m s}^{-1}$ velocity shifted to south-southwest at $1\text{--}2\text{ m s}^{-1}$. Peak ozone concentrations of 130 ppb on July 10 and 170 ppb on 11 July at 15 h LST were then measured at the National Observatory (Güsten et al., 1988). At the same time, similar high ozone concentrations were monitored on the Hill of Lykabetos. The same events occurred from July 15 to 18, when at 12 h LST the wind shifted from NNE to SSW at $1\text{--}2.5\text{ m s}^{-1}$ for four days in total. Accordingly, ozone concentrations above 120 ppb were recorded again during these days between 13 and 17 LST. This smog period ended early in the morning on 19 July at 4 h LST, when the southerly winds changed to NNE and continued to blow in that direction for more than a week. During that week ozone concentrations in central Athens did not exceed 80 ppb at any time of the day. All the photochemical smog episodes, also those in August 1984, occurred under meteorological conditions of high insolation, high temperature and with relatively little ($2\text{--}4\text{ m s}^{-1}$) southerly flow during the day-time and with a northerly flow at night and in the early morning. This is the typical pattern of sea-land breeze circulation. The interrelationship of smog episodes with the sea breeze circulation is demonstrated in Fig. 4 showing the ozone concentrations at site K on the shoreline and on the island of Aegina (site A, Fig. 2), measured on 1 August, 1984. On that day, the northerly background flow was of significant magnitude so that the sea breeze was not able to overcome it. Thus, during the whole night of 31 July and the morning of 1 August, emissions from the city were advected out to the Gulf of Saronikos and the ozone concentrations at site K were low. Over the sea, the NO_x and hydrocarbons from anthropogenic sources inside the Greater Athens basin find favourable conditions to generate and retain high ozone and PAN concentrations (Demerjian et al., 1974; Güsten, 1986). Such conditions include the lack of catalytic surfaces and of fast acting sinks to destroy ozone as well as smaller vertical transport coefficients

(Aldiz, 1969). Around noon, when the sea breeze sets in, the air-mass with the photochemically produced ozone and other oxidants formed over the Gulf of Saronikos are re-advected towards the shore and the concentrations of ozone on the island of Aegina and at site K reach 65 to 80 ppb in the early afternoon (Fig. 4). In Fig. 4 the sudden increases in ozone concentration at sites A and K are shown together with the wind shift from NNW to SSW. The ozone measured at site A is mostly the product of photochemistry over the sea. The island of Aegina, 30 km from the center of Athens, is a rural island where NO and reactive hydrocarbons are locally negligible. Thus, these primary pollutants must be due to sources in Athens. During one of the sea breeze events with high ozone concentrations a peak ozone concentration of 125 ppb was measured on the rural island of Aegina.

A similar rise in local ozone concentrations measured on two consecutive days is depicted in Fig. 5. It shows that with northerly winds the high ozone concentrations decline and southerly winds bring the ozone concentration up to nearly 100 ppb at the coast near Kastella. During smog episodes the ozone level in the city of Athens often remains high throughout the night. At night, when the land surface usually cools faster than the neighbouring sea, the inverse phenomenon of sea breeze is observed, namely land breeze circulation. Together with the prevailing synoptic wind from NE the Athens basin is ventilated and the air pollutants from the night and early morning rush hour start the photochemical smog cycles over the Gulf of Saronikos again. When the prevailing synoptic wind from NE is strong enough, the sea breeze from SW cannot overcome it. During these days the ozone levels in central Athens remain fairly low, generally below 80 ppb.

The interrelationship of photo-smog episodes with sea breeze events was first described by Mukammal (1965). He observed on the shore of Lake Erie tobacco injury, so-called "weather flecks" caused by photochemically produced ozone. Mukammal (1965) made the sea breeze responsible which re-advected air masses containing ozone from industrial areas to the coast.

CONCLUSION

The measurement campaigns performed in Greater Athens demonstrate the advection of pollutants to and from the Gulf of Saronikos and the generation of large amounts of ozone and PAN over water in the photo-smog process. Photo-smog episodes in Greater Athens are accompanied by well-developed sea breezes. The local ozone and PAN concentrations measured in central Athens in the afternoon are a function of the primary pollutant concentration advected to the Gulf of Saronikos but also of the length of time available to generate photo-smog

over the sea. On days, when the onset of the sea breeze is early enough (typically around 9 h), the reaction time is limited. As a consequence, the ozone and PAN concentrations in central Athens are low. Later in the year, in June until September, when the sea breeze is retarded by 2-3 h, the concentration levels of central Athens rise in the afternoon and exceed the U.S. Air Quality Standard. Thus, considerable motion of the photochemical smog and its vertical mixing need to be taken into account in designing pollution reduction strategies in downtown Athens.

Acknowledgement

This work was performed under the auspices of the Greek-German Scientific Cooperation Agreements. The financial support by the Greek Ministry of Research and Technology and of the Internationales Büro of the Forschungsanlage Jülich (KFA) is gratefully acknowledged.

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FORMATION OF PHOTOCHEMICAL SMOG

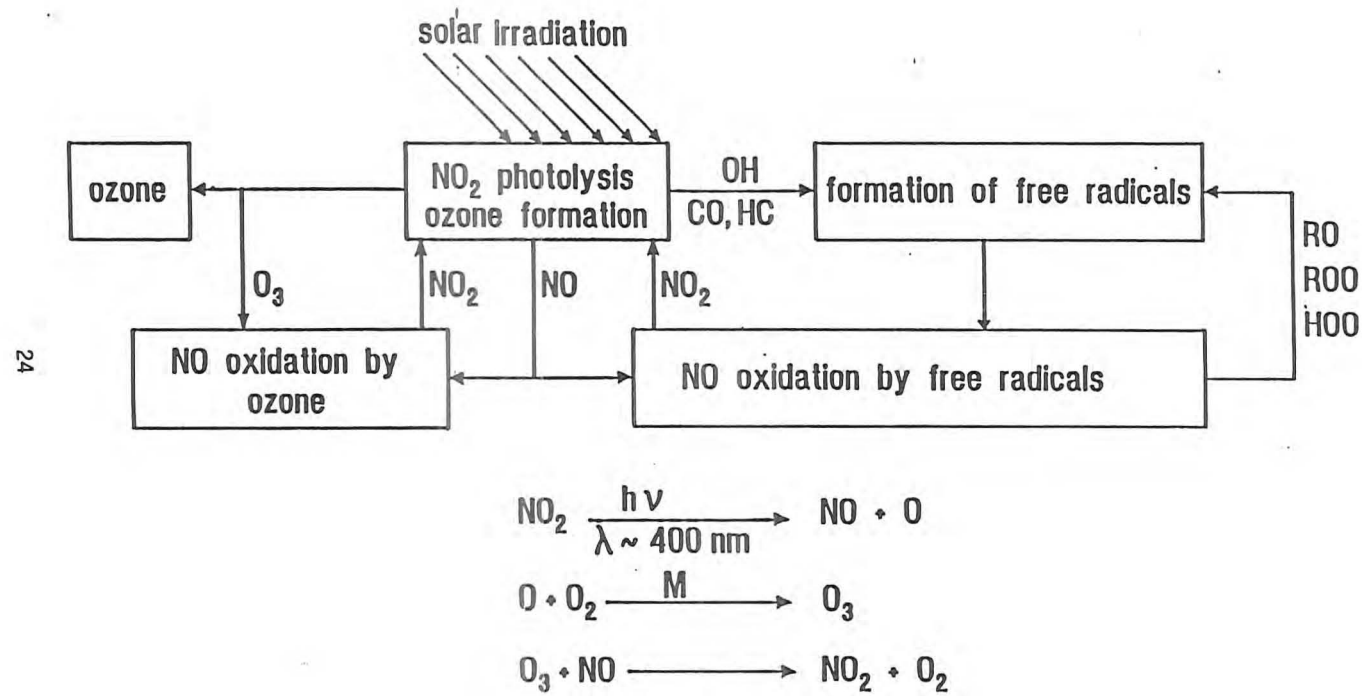


Fig. 1

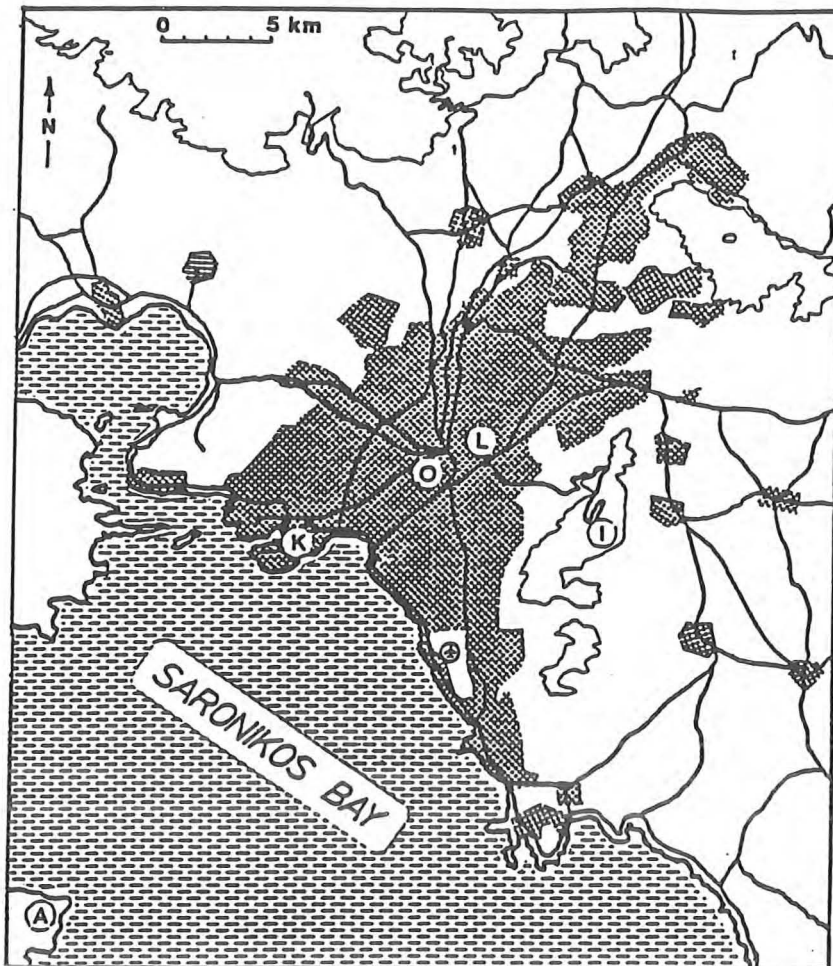


Fig. 2: Map of Greater Athens with the ozone monitoring sites

- O = National Observatory of Athens (107 m above MSL),
- L = Hill of Lykabetos (\approx 200 m above MSL),
- I = Mount Immitos (\approx 1000 m above MSL)
- K = Kastella on the shoreline,
- A = Island of Aegina (\approx 200 m above MSL).

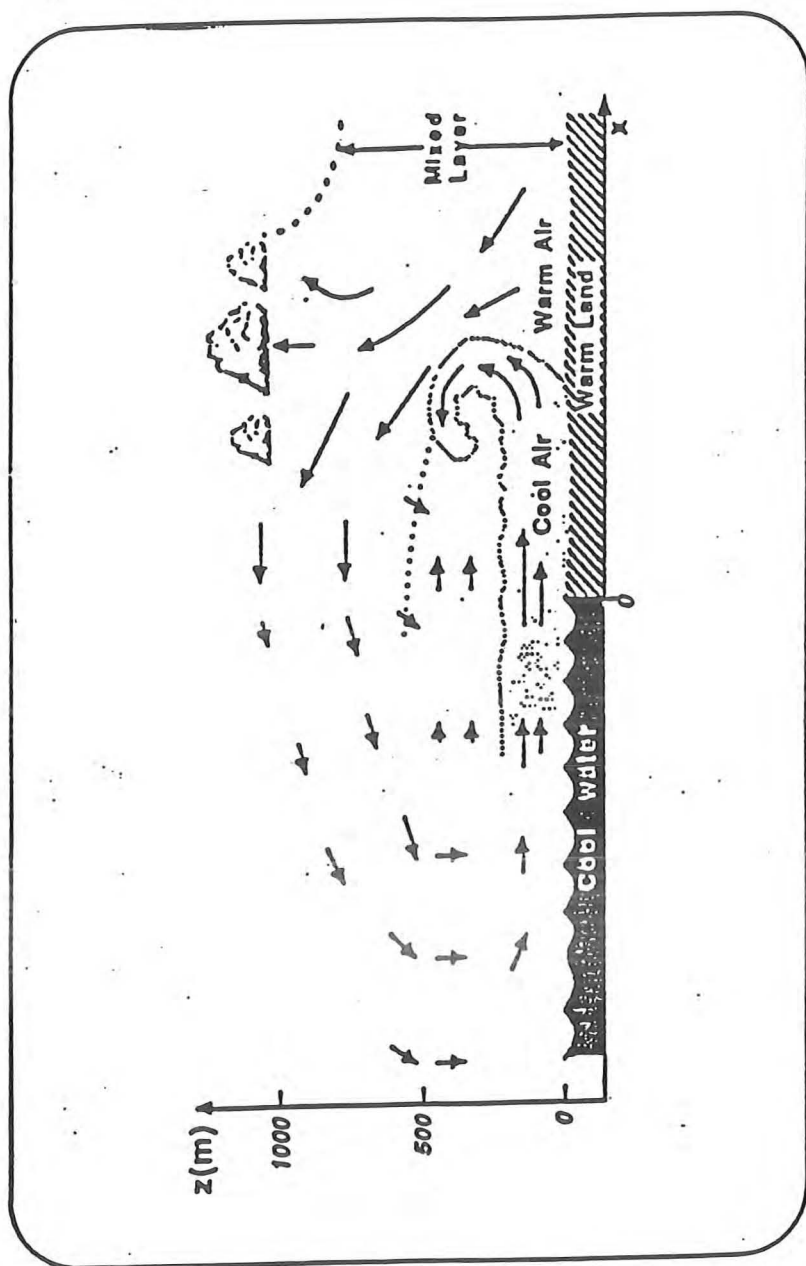


Fig. 3: Sea breeze circulation

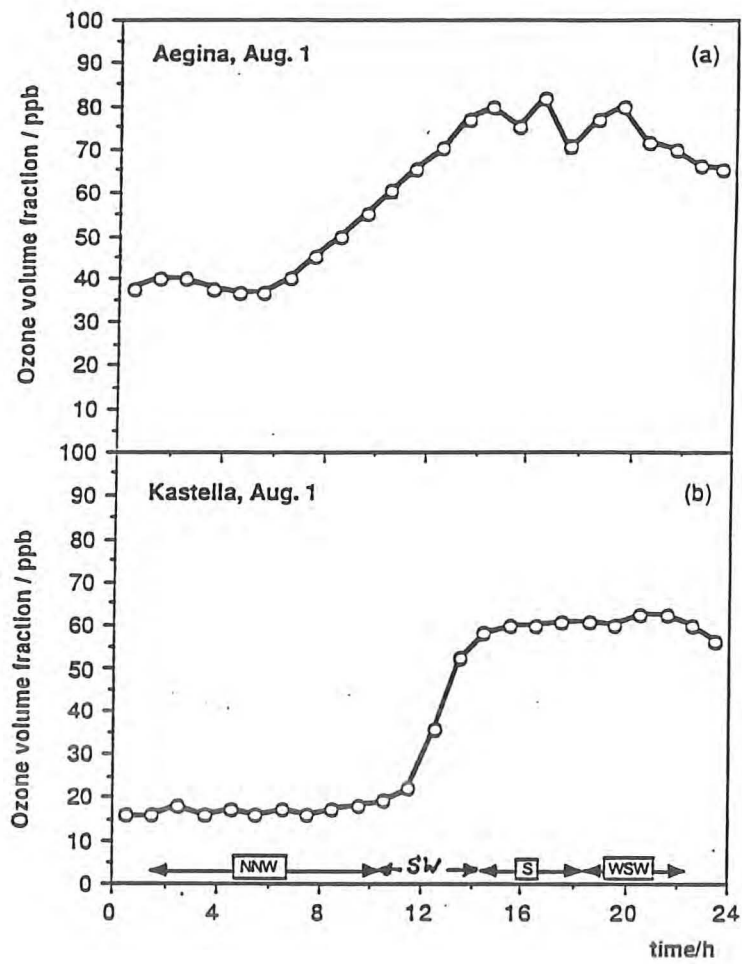


Fig. 4: Diurnal variation of the volume fraction of ozone at the measuring sites on Aegina and in Kastella on 1 August, 1984.

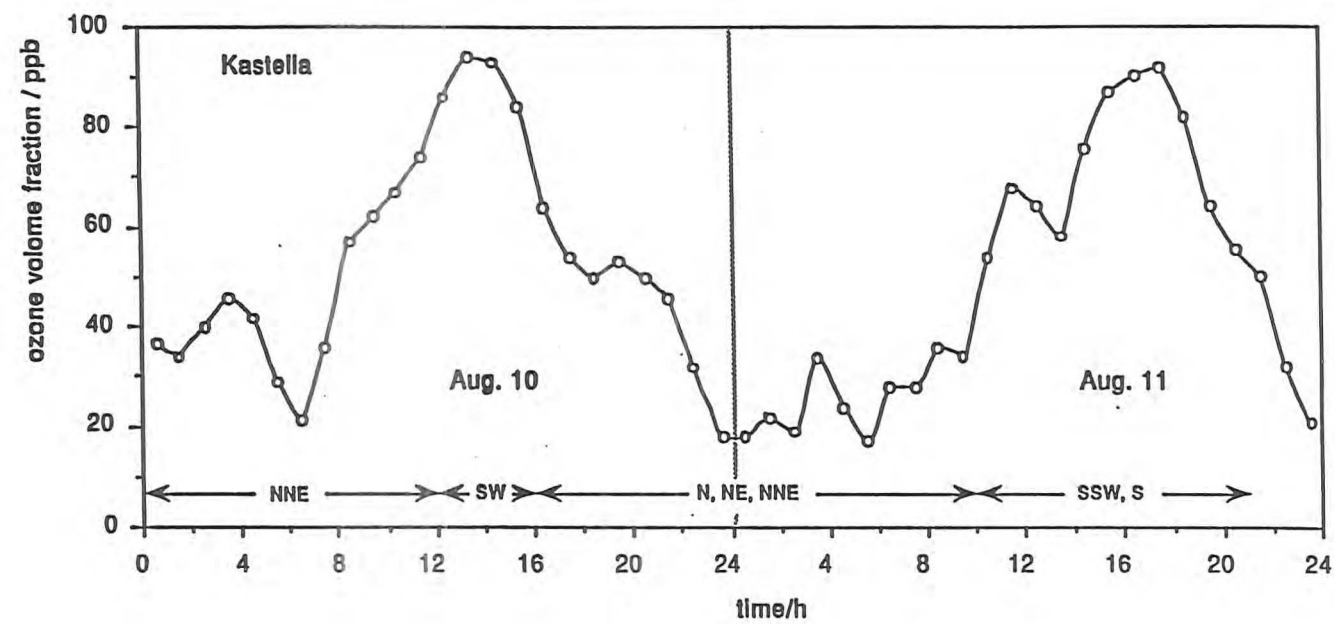


Fig. 5: Diurnal variation of the ozone concentration at the measuring site in Kastella at the coast on August 10 and 11.

Modelling of Atmospheric Transport Phenomena in Athens

N. Moussiopoulos

ABSTRACT

The steady increase of the air pollution levels in Athens proves the necessity for a long-term pollution abatement strategy based on reasonable measures. Given that the Athenian smog is of primarily photochemical nature, these measures should above all aim at reducing the emissions of motorcars, which are definitely the main sources for all major photosmog precursors. An advanced air pollution abatement strategy should allow to check the effectiveness of pollution abatement measures in terms of the resulting decrease in pollution levels. Apparently, for such a strategy reliable mathematical models are required for simulations of the mesoscale flow and the dispersion of chemically reacting pollutants.

The present paper deals with the application of the nonhydrostatic mesoscale model MEMO and the dispersion/transformation model MARS for the description of the formation of photochemical smog in Athens. Both models are currently being used within the EUREKA environmental project EUROTRAC.

The results for the mesoscale flow in the Attica peninsula reveal the significance of thermally driven local circulation systems, primarily of the sea breeze, with regard to the pollutant transport mechanism in the Athenian atmosphere (Figure 1). The analysis of these results allows to identify the reasons for the trapping of pollutants above Athens in the case of high pollution episodes, namely the occurrence of intense temperature inversions and recirculation phenomena associated with the local circulation systems.

The predicted photochemical pollutant concentrations (Figures 2 and 3) elucidate the characteristics of the Athenian photosmog, notably an intense early morning photochemical activity above the sea close to the shoreline, a contribution of the daytime transport by the sea breeze to the downtown ozone formation, a sharp increase of ozone with height associated with high surface emissions of nitric oxide, ozone levels in the suburban periphery of Athens exceeding those in the city centre and the participation of emissions originating from industrial areas outside the Athens basin to photochemical reactions in the Athens basin.

* in the framework of the scientific cooperation between the Federal Republic of Germany and Greece, Thessaloniki, October 9, 1990.

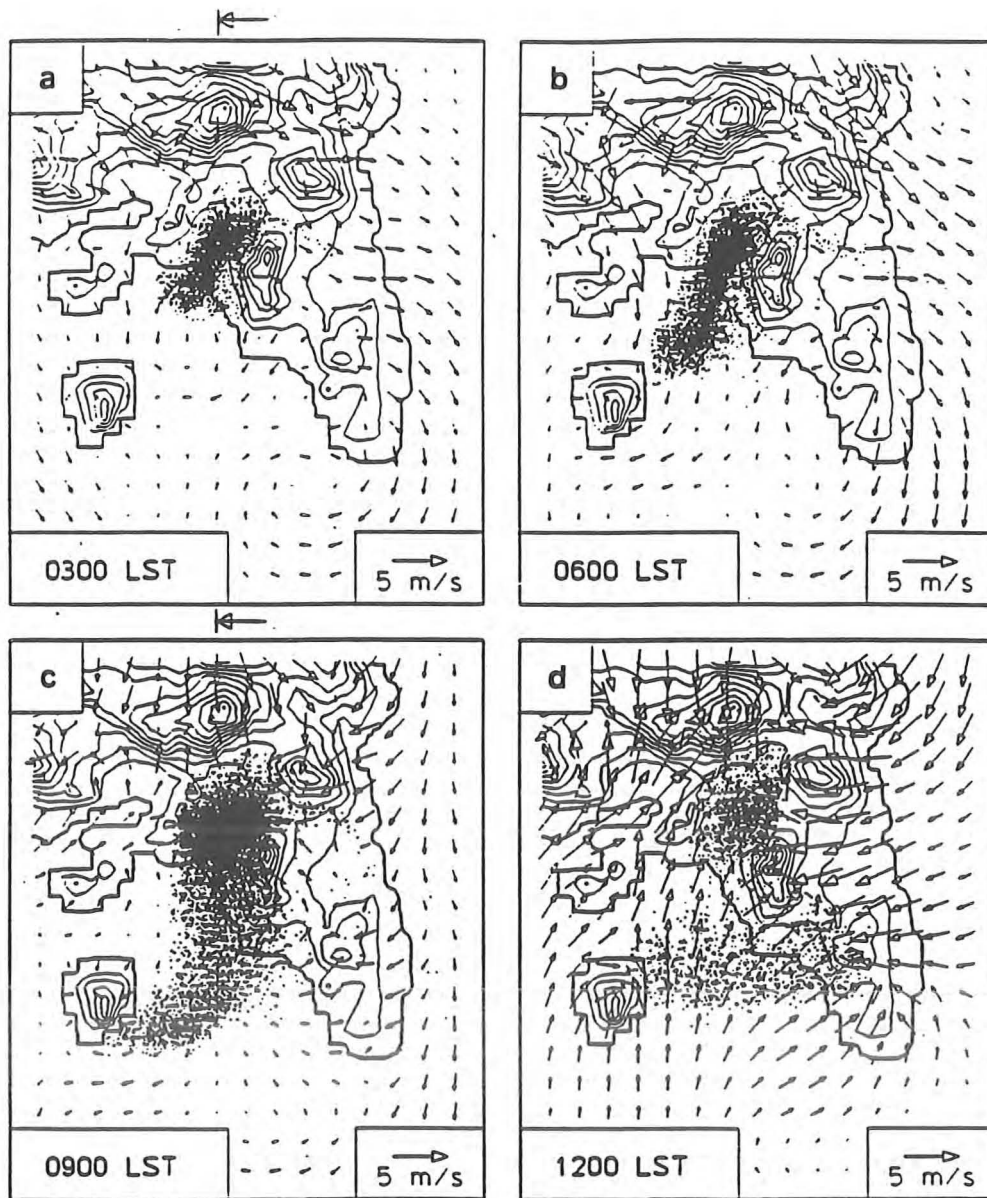


Figure 1 Results of the nonhydrostatic model MEMO for the diurnal variation of the surface level wind flow and the surface level concentration of carbon monoxide in the Greater Athens Area.

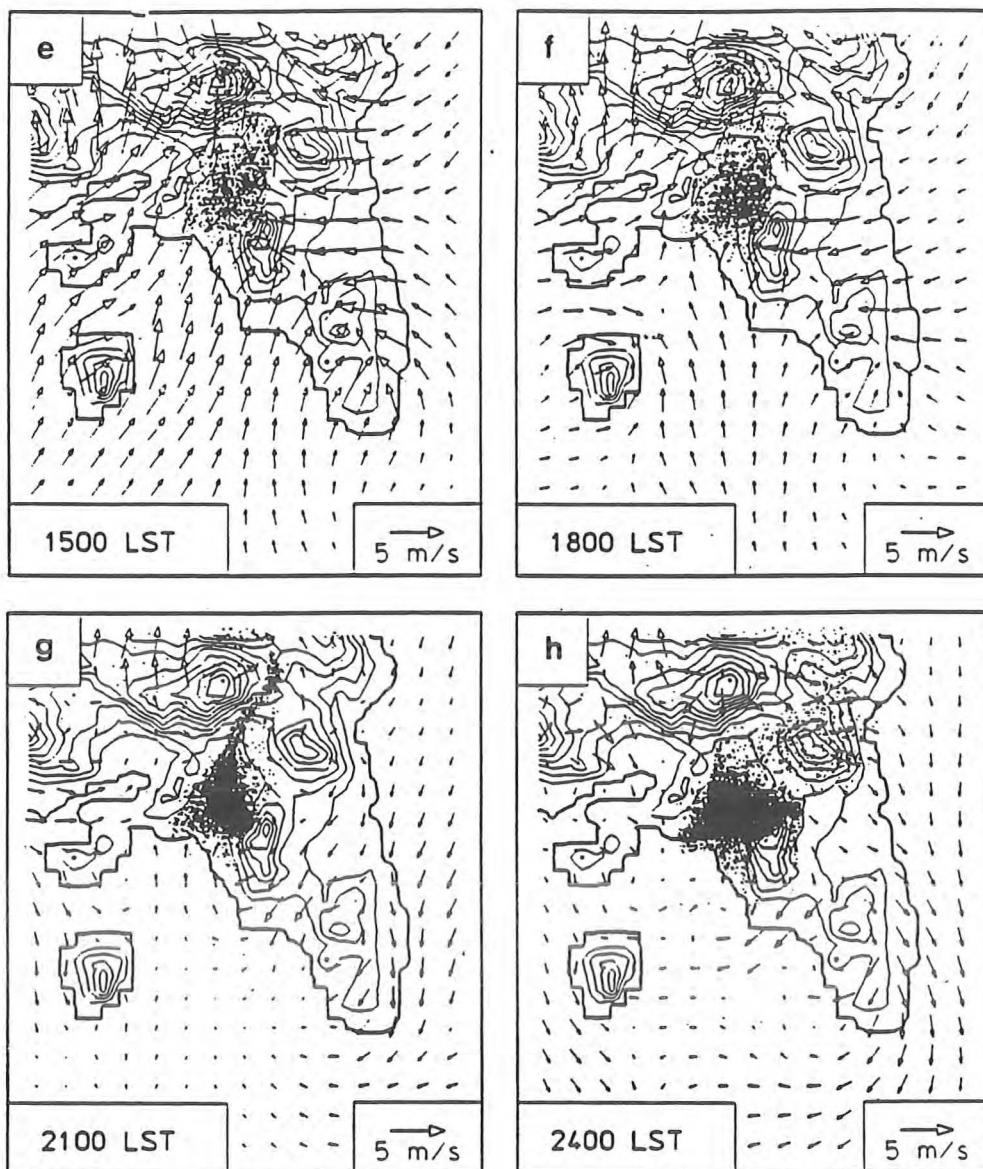


Figure 1 (Continued)

NO (ppb)

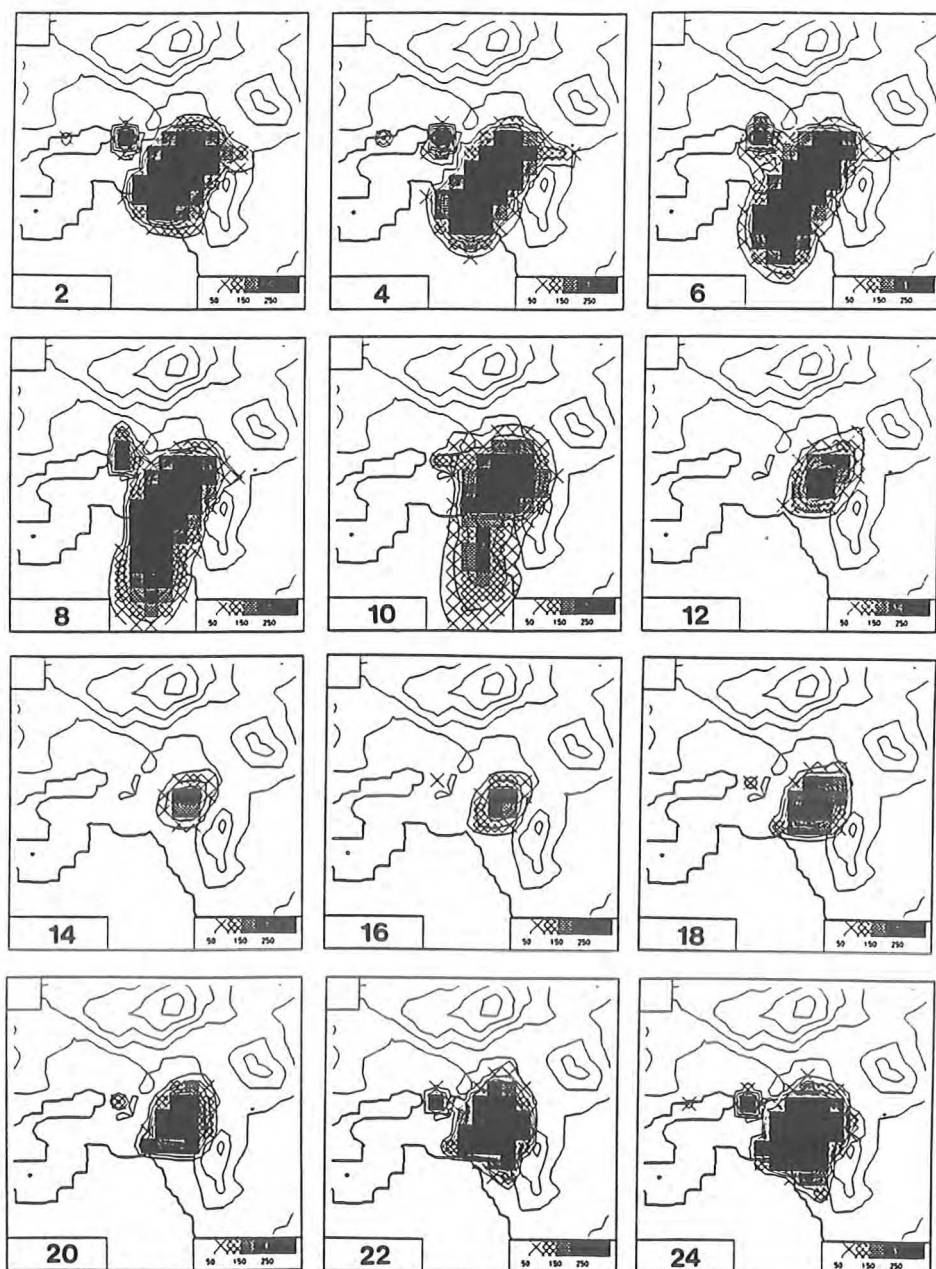


Figure 2 Results of the dispersion/transformation model MARS for the diurnal variation of the surface level concentration of nitric oxide in the Greater Athens Area.

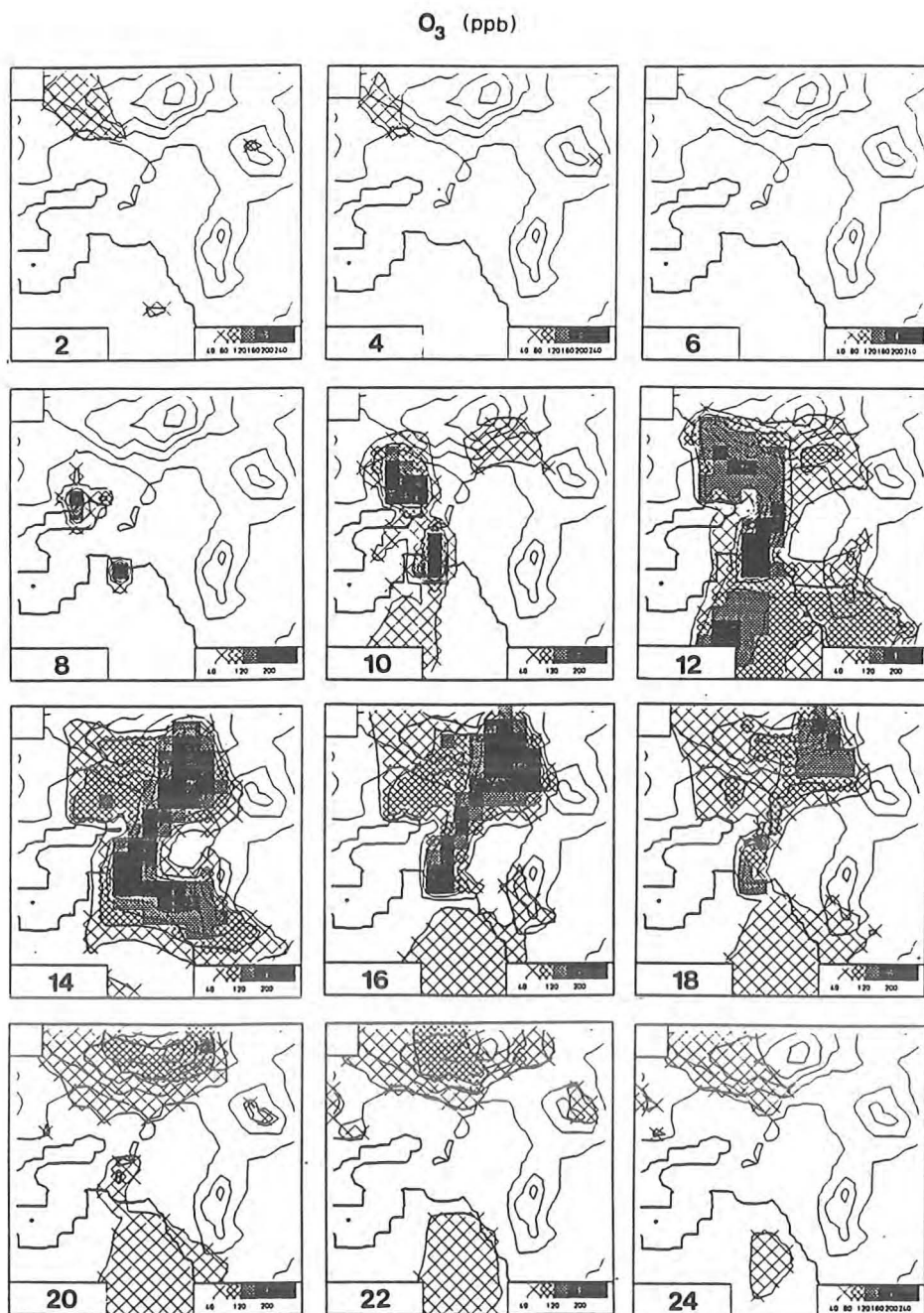


Figure 3 Results of the dispersion/transformation model MARS for the diurnal variation of the surface level concentration of ozone in the Greater Athens Area.

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Immission Measuring Techniques

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Abstract

Continuously analyzing immission measuring techniques for those trace gases which play the dominant role in the formation of photochemical smog are reviewed. These trace gases are hydrocarbons, nitrogen oxides and ozone.

Introduction

Continuously analyzing means that the air flow with the sample gas is brought directly to a physical measuring device which works automatically without manually generated interrupts, as normally used by wet chemical measuring techniques. The requirements which should be fulfilled by such devices are :

- representative sample intake without losses in the sampling manifold
- high sensitivity, better than 1% of a limiting value
- high accuracy, better than 1 % of full scale
- high selectivity for the analyzed trace gas without interference by other gases
- long time stability
- possibility of calibration
- little attendance

Measuring Techniques

1. Hydrocarbons

It would be very useful to have an instrument which discriminate between the olefinic hydrocarbons which are responsible for the formation of photochemical smog and all other hydrocarbons. Unfortunately this cannot be done with commercially available instruments. These instruments can only subtract the amount of natural methane (about 1.7 ppm) from the total concentration of hydrocarbons.

The schematic diagram of a hydrocarbon monitor is given in fig. 1. A pump aspirates from the sample line the gas to be analyzed. A small part of it is conveyed at constant flow rate to the analyzer, whereas the rest is vented.

The gas portion to be analyzed is sent to a flame ionisation detector (FID) either directly or through a special scrubber which removes all the hydrocarbons except methane. The scrubber

consists of a special catalytic reactor kept at constant temperature.

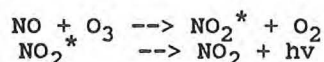
The built in microprocessor provides cyclically the scrubber actuation. The obtained response, related to methane contents only, is subtracted from the total response.

The FID uses the fact that the electrical conductivity of a hydrogen-air flame is strongly increased by small amounts of hydrocarbons reaching the zone of this flame.

A simplified diagram of the flame ionisation detector is shown in fig. 2. Hydrogen und air are conveyed to the burner. Without hydrocarbons in the burner cell there is only a small electrical current moving from the cathode to the anode. With hydrocarbons present in the flame there is an increase in conductivity resulting in an increase of the current which can be measured with a suitable recorder.

2. Nitrogen oxides

The chemiluminescent reaction of NO and O₃ provides the basis for the instruments to measure nitrogen oxides.



Light emission results when electronically excited NO₂ molecules revert to their ground state.

A schematic diagram of a nitrogen oxides monitor is shown in fig. 3. To measure NO concentrations, the gas sample to be analyzed is mixed with O₃ in a reaction chamber. The resulting chemiluminescence is monitored through an optical filter by a high sensitive photomultiplier positioned at one end of the reaction chamber.

The filter/photomultiplier combination responds to light in a narrow wavelength band unique to the reaction mentioned excluding any interference. The output from the photomultiplier is proportional to the NO concentration.

To measure the NO_x concentration (NO + NO₂), the sample gas flow is diverted through an NO₂ to NO converter. The chemiluminescent response in the reaction cell to the converter effluent is then proportional to the NO_x concentration entering the converter. Since this is not an absolute analytical method calibration is necessary.

3. Ozone

Commercially available ozone analyzers operate either on the principle of photometric detection of the absorption of UV-light or on the chemiluminescent light resulting from the flameless gas phase reaction between ethylene and ozone. Typically used ozone analyzers are shown in fig. 4,5.

The UV-absorption measurement technique is based on the capability of ozone to absorb certain wavelengths of ultraviolet radiation at 254 nm.

This absorption follows the law of Lambert-Beer:

$$I_T = I_0 e^{-\beta c l}$$

$$\ln(I_0/I_T) = \beta c l = E$$

E = absorbance

β = absorption coefficient

l = path length

c = concentration

The ozone analyzer measures alternately ambient air with ozone and ambient air without ozone. Ozone free air is achieved through an ozone scrubber. The valves for the two paths is operated by a microprocessor. The difference between the two responses I_T and I_0 is the absorption due to ozone. The microprocessor solves the Lambert-Beer relationship to output ozone concentrations or mixing ratios.

Some ozone analyzers can be equipped with an ozone generator for calibration of the instrument. Accurate ozone concentrations are generated when oxygen present in clean air is exposed to short wavelength UV-radiation at 185 nm.

Concerning ozone analyzer using the chemiluminescence method, air and ethylene are drawn into a temperature reaction chamber that contains an optically flat window mounted at the front side of a photomultiplier tube.

If ozone is present in the sample air stream, its flameless reaction with ethylene results in the emission of photons which are recorded as an increase of the electric current from the photomultiplier tube. This increase in signal current is detected and amplified by an electrometer whose output is fed to signal conditioning buffer amplifiers.

The amplifier drive the front panel meter and the electrical output for recording.

The photomultiplier tube is contained in a thermoelectrically cooled housing which is temperature regulated to $25\text{ }^{\circ}\text{C} \pm .1\text{ }^{\circ}\text{C}$. This is necessary to insure that short and long term drift problems due to changes in ambient temperature are minimized.

The analyzer must be calibrated, because the response is only relative with respect to ozone concentration.

In cooperation with the University of Bonn we have developed a small, light weight (1,5 kg) and fast response ozone sensor on the basis of a chemiluminescence reaction too. But in this case the reaction takes place between ozone and a selected organic dye which is adsorbed on silica gel. This dye emits strong chemiluminescence in the blue wavelength range (450 nm) which can be monitored with a cheap and small photomultiplier.

The schematic diagram of this instrument is shown fig. 6. The advantage of this instrument is its high sensitivity with a detection limit of 10 ppt and its fast response time of about 0,1 s which is necessary for ozone measurements with planes or balloons.

Table 1 gives a summary about the measuring ranges, the detection limits and the response times of the instruments mentioned in this review.

Table 1: Properties of emission measuring techniques

trace gas (method)	range	detection limit	response time (90 %)
O ₃ (UV-absorption)	0-1 ppm	1 ppb	25 s
O ₃ (chemiluminescence, gas-gas)	0-1 ppm	1 ppb	10 s
O ₃ (chemiluminescence, gas-solid)	0-1 ppm	10 ppt	60 ms
NO _x (chemiluminescence)	0-5 ppm	6 ppb	3 s
C _n H _n (FID)	0-100 ppm	10 ppb	4 s

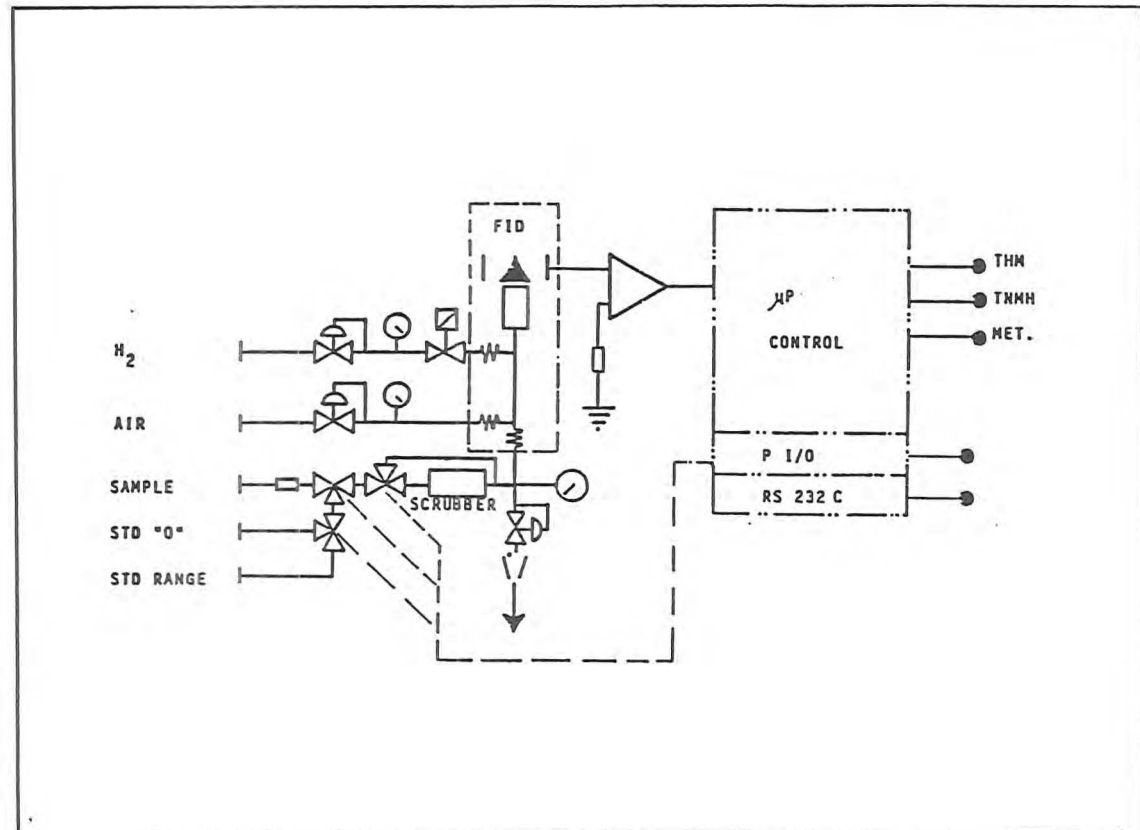


Figure 1: Schematic diagram of a hydrocarbon monitor

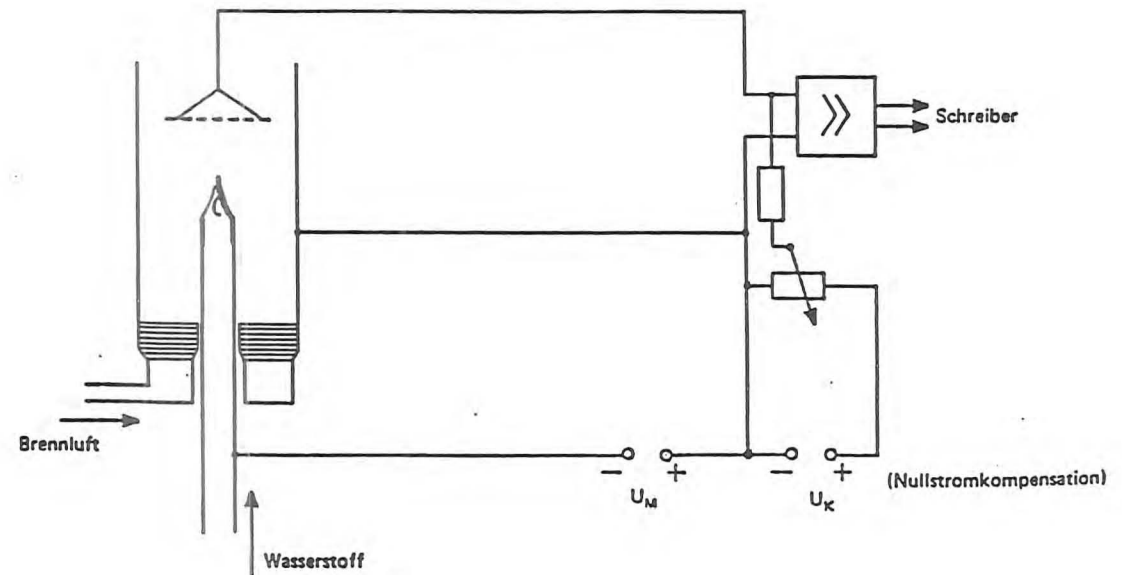


Figure 2: Flame ionisation detector (FID)

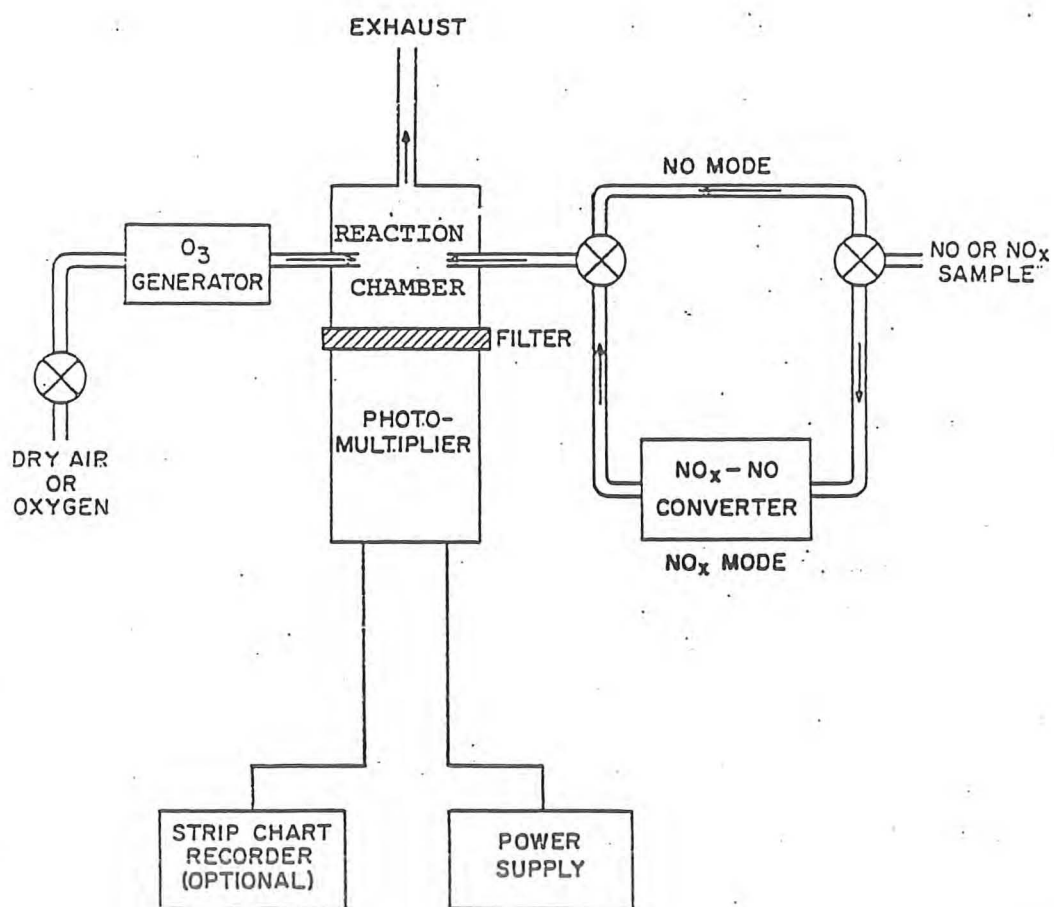


Figure 3: Chemiluminescence analyzer for nitrogen oxides (NO, NO_x)

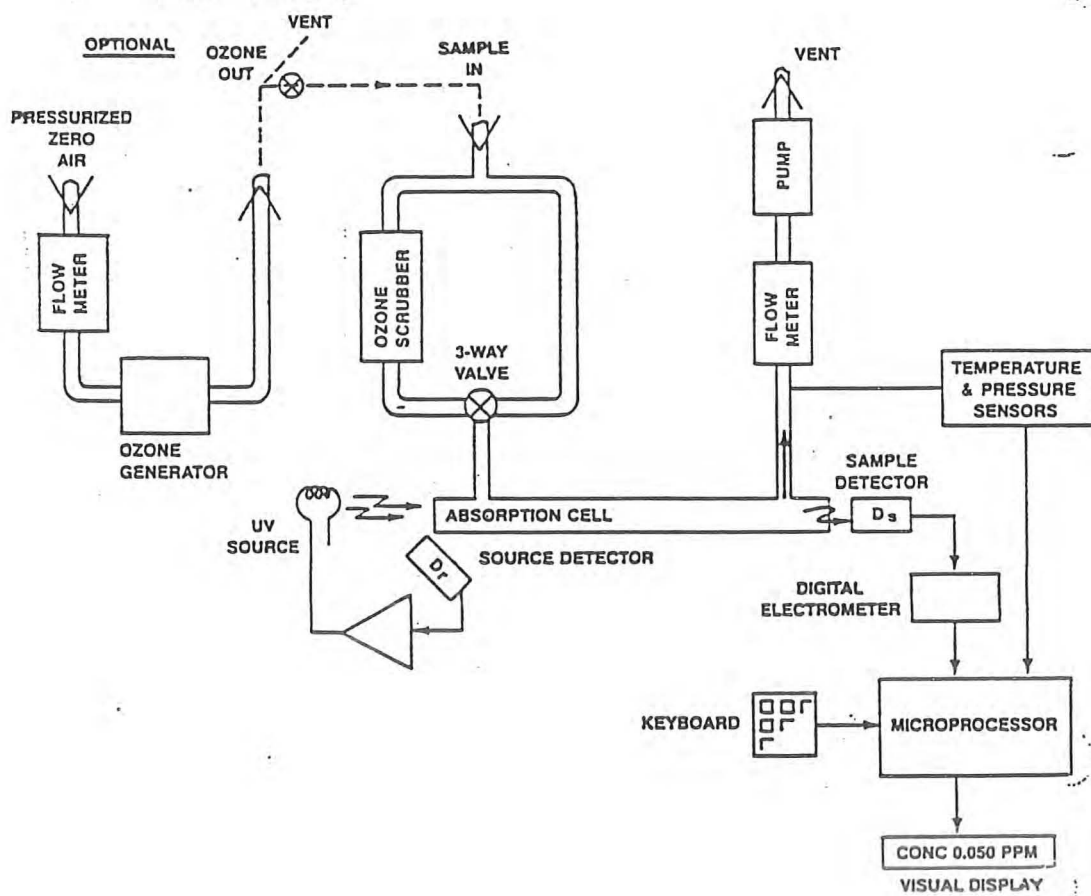


Figure 4: UV - absorption ozone analyzer

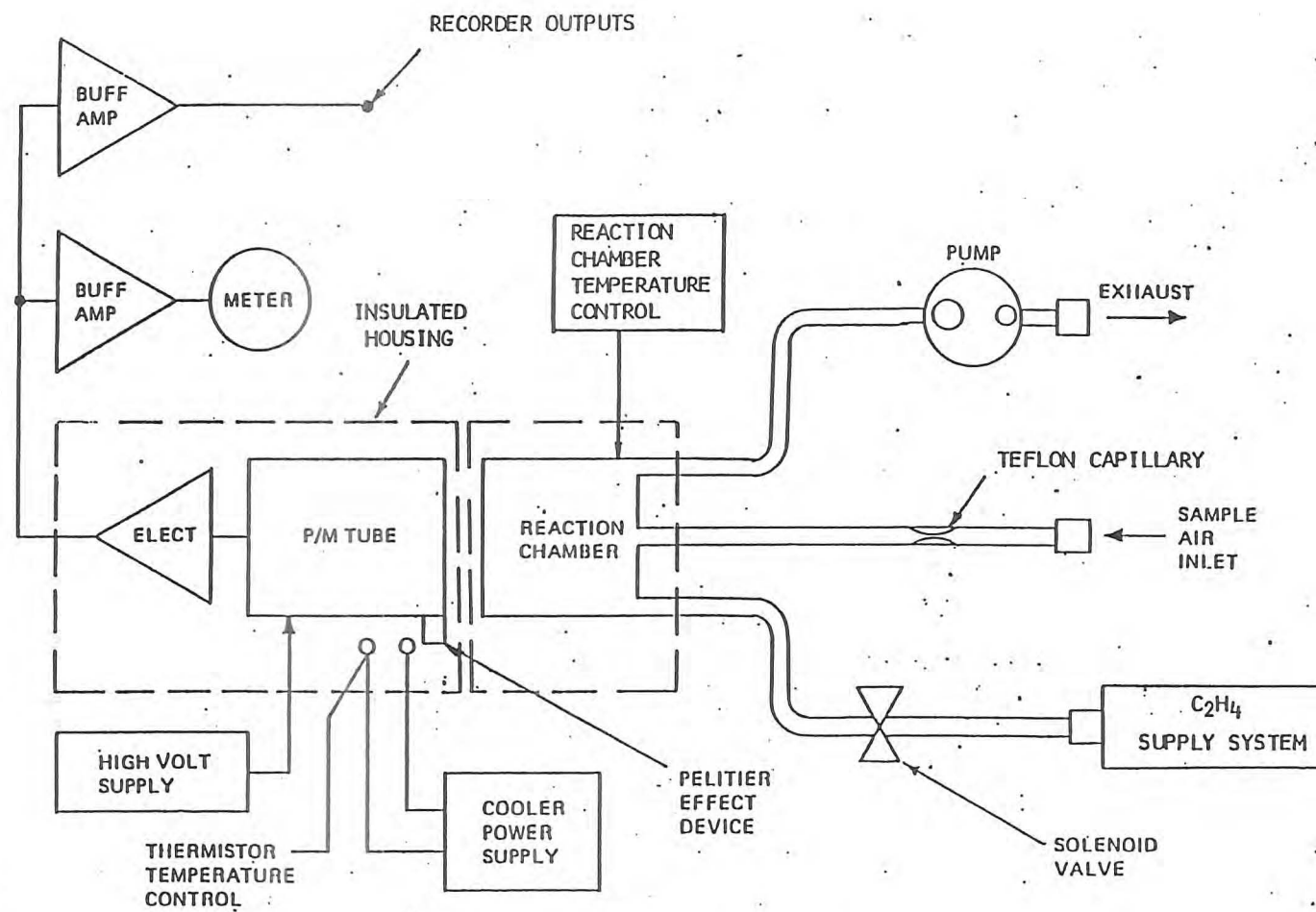


Figure 5: Chemiluminescence ozone analyzer.

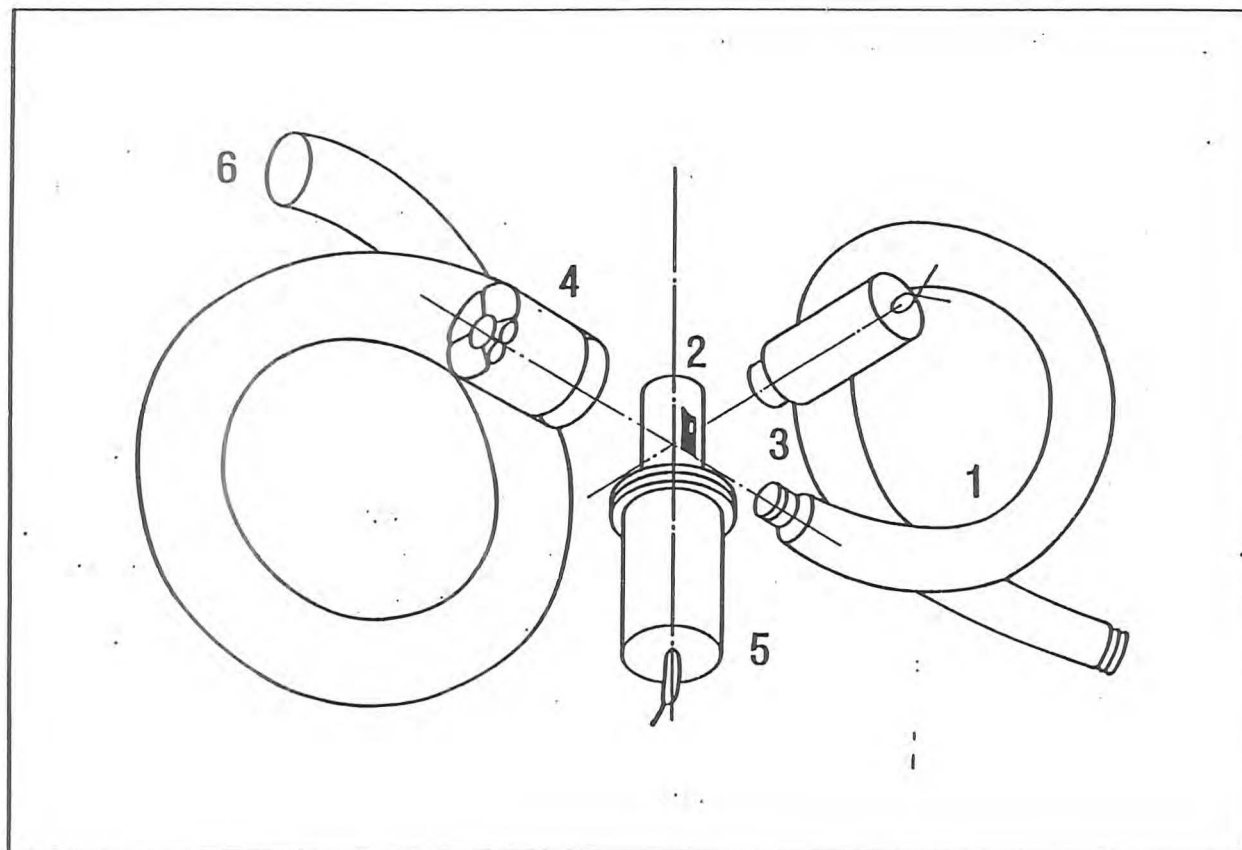


Figure 6: Fast response chemiluminescence ozone analyzer

1: sample inlet tube, 2: photomultiplier, 3: ozone sensor, 4: fan,
5: photomultiplier housing, 6: sample outlet tube

Laboratory Measurements of Automotive Exhaust Emissions

N. A. Kyriakis.

The aim of the presentation was to give an idea of the capabilities and the experience of the Laboratory of Applied Thermodynamics, University of Thessaloniki, as far as automotive exhaust emissions are concerned.

The basic analytical equipment consists of CO₂ and CO (NDIR) analysers (2 items for each component), HC (FID) analysers (2 items), NO_x (CLD) analysers (2 items) and O₂ (paramagnetic) analyser (1 item). There are also two fuel rating engines (cetane number for diesel fuels, octane number for otto fuels).

One chassis dynamometer with eddy current brake (max.power 130 kW, max car speed 200 km/h) capable to simulate any driving pattern and two engine brakes (in test cell) both with max power 130 kW and max brake speed 10000 rpm are the braking capabilities of the Laboratory.

There is a complete installation for car exhaust emission measurement according to the ECE 15-03 (undiluted gas) and the ECE 15-04 or FTP-C/H (diluted gas) regulations.

The major experimental research projects undertaken by the Laboratory of Applied Thermodynamics are as follows (Title; Time Period and Summary):

1.) Exhaust Emission Study of the Current Vehicle Fleet in Athens (Phases I & II) in 1983/84)

Sponsored by the EEC (DG XI) and the Greek Government, emission factors were derived for each vehicle category. A sample of 500 passenger cars was measured according to the ECE 15-03 test procedure and the relevant emission factors were derived for this vehicle category. The ATHENS 83 driving pattern was derived, based on speed recordings on the most significant roads of the area. Total recording duration 5000 km.

(2) Determination of the Area and Time Distribution of the Pollutant Emission and Fuel Consumption due to Traffic in the Thessaloniki Area (1988/90).

Sponsored by the Greek Government (Thessaloniki Organization), the driving pattern of the city was developed. The influence of the hour of the day on the driving pattern was investigated. A sample of 100 passenger cars was measured, according to the ECE 15-04 test procedure and the relevant emission factors were derived. Time distribution of the pollutant emission and fuel consumption was estimated, based on the time dependency of the driving pattern and the COPERT computer programme developed by the Laboratory for the EEC.

3.) Installation of Diesel Particulate Trap Oxidisers on Athens Urban Buses (1985/90).

Sponsored by the Greek Government, a trap oxidiser system, using exhaust gas throttling as the main regeneration system, coupled to a by-pass control of ceramic temperature, was installed on five experimental buses of the Athens bus fleet. Cerium Naphthenate was also used as fuel additive at varying concentrations, in order to ensure safe and reliable regeneration at relatively low temperatures. The behaviour of the systems was constantly monitored through data loggers during regular on-road operation. Today, 110 buses in Athens area are equipped with the trap system and some 80000 km are already accumulated on the oldest one, without any operation trouble. The Greek government has already decided to equip the whole fleet of Athens urban buses with the system.

Estimation of Emission Data as Input for Long Range Transport Calculations.

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Abstract

For the 3D-photochemical atmospheric transport model (CTM) developed by the EURAD-project of which the object is to investigate and forecast the atmospheric ozone and acid deposition in Europe an emission inventory is elaborated for SO_2 , NO_2 , and Volatile Organic Compounds (VOC).

The anthropogenic emission of SO_2 , NO_2 , and VOC is governed by consumption of energy, by the composition of fossile fuels used and by the mode of use. Therefore, from the energy balance estimates can be made on emission of pollutants. From the annual emission data available on national level the emissions are calculated in each of the grid elements used by the CTM (80 by 80 km^2) covering Central Europe assuming that the emission is proportional to population density. Cities are considered as point sources of which the emissions are proportional to their population number. The rest of the total emission is distributed uniformly on the rural area taking in account the percentage of land in each grid element (Ref.2).

For SO_2 the emission from power plants is estimated from installed capacity. For NO_2 and VOC also the long distance road traffic is considered. The roads are considered as straight lines between the cities, and the line emission or the traffic volume is assumed to be proportional to the population number of the connected cities. The natural VOC emission is considered to be proportional to forest density using specific national splitting factors for the ratio between anthropogenic and natural emission (Ref.4).

This first estimate of the distribution of emission serves as a rough model for countries where no data are available. By introducing known emission sources and handling the rest of the total emission as described the data base is improved step by step.

Especially the estimated spatial distribution in Greece is shown using data from N.Moussiopoulos and Z.Samaras (Ref.6).

SO_2 -emission.

According to the simple model calculation with the emission data proportional to population number as described above the total SO_2 -emission in Greece in 1985 of 500 kt (Ref.6) is specified in

1. urban emission 63.6 kt/a
2. rural emission 75.7 kt/a
3. power plants 360.7 kt/a

The highest contributions to urban emission according to inhabitant numbers come from Athens (47 kt/a) and Thessaloniki (10 kt/a). From the total size of $1.3 \cdot 10^5$ sqkm we have about $0.93 \cdot 10^5$ sqkm rural area which gives a specific emission of $5.84 \cdot 10^{-4}$ kt/a/sqkm and 3.7 kt/a in a 6400 sqkm grid element. The contribution to the emission from power plants comes from Demetrius (96 kt/a) and Kardias (88.3 kt/a) and from Amyntaion (48 kt/a) and Ptolemais (49.6 kt/a) leading to 184.3 kt/a and 97.6 kt/a in two grid elements in northern Greece.

I.e. the total emission mainly comes from the power plants in northern Greece and to a smaller amount from the power plants in Peleponnes and from the power plant Aliveri (26 kt/a) and domestic emission from Athens (Fig.1).

NO₂-emission.

Calculated from the model the total NO₂-emission in Greece in 1985 of 308 kt (Ref.6) is spezified in

1. urban emission 26.9 kt/a
2. rural emission 32.1 kt/a
3. traffic emission 102 kt/a
4. power plants 146.8 kt/a

The highest contributions to urban emission according to inhabitant numbers again come from Athens (20 kt/a) and Thessaloniki (4.2 kt/a). The specific rural emission is $2.47 \cdot 10^{-4}$ kt/a/sqkm and 1.58 kt/a in a 6400 sqkm grid square. The traffic emission mainly comes from Athens (45.1 kt/a) and to some extend from Thessaloniki and Kriti. The contribution to the emission from power plants again comes from Demetrius (31.2 kt/a) and Kardias (28.7 kt/a) and from Amyntaion (15.6 kt/a) and Ptolemais (16.1 kt/a) leeding to 60 kt/a and 31.7 kt/a in northern Greece.

I.e. the total emission mainly comes from the power plants in northern Greece and from traffic in the region of Athens (Fig.2).

VOC-emission.

Calculated from the model the total VOC-emission in Greece in 1985 of 612 kt (Ref.6) is spezified in

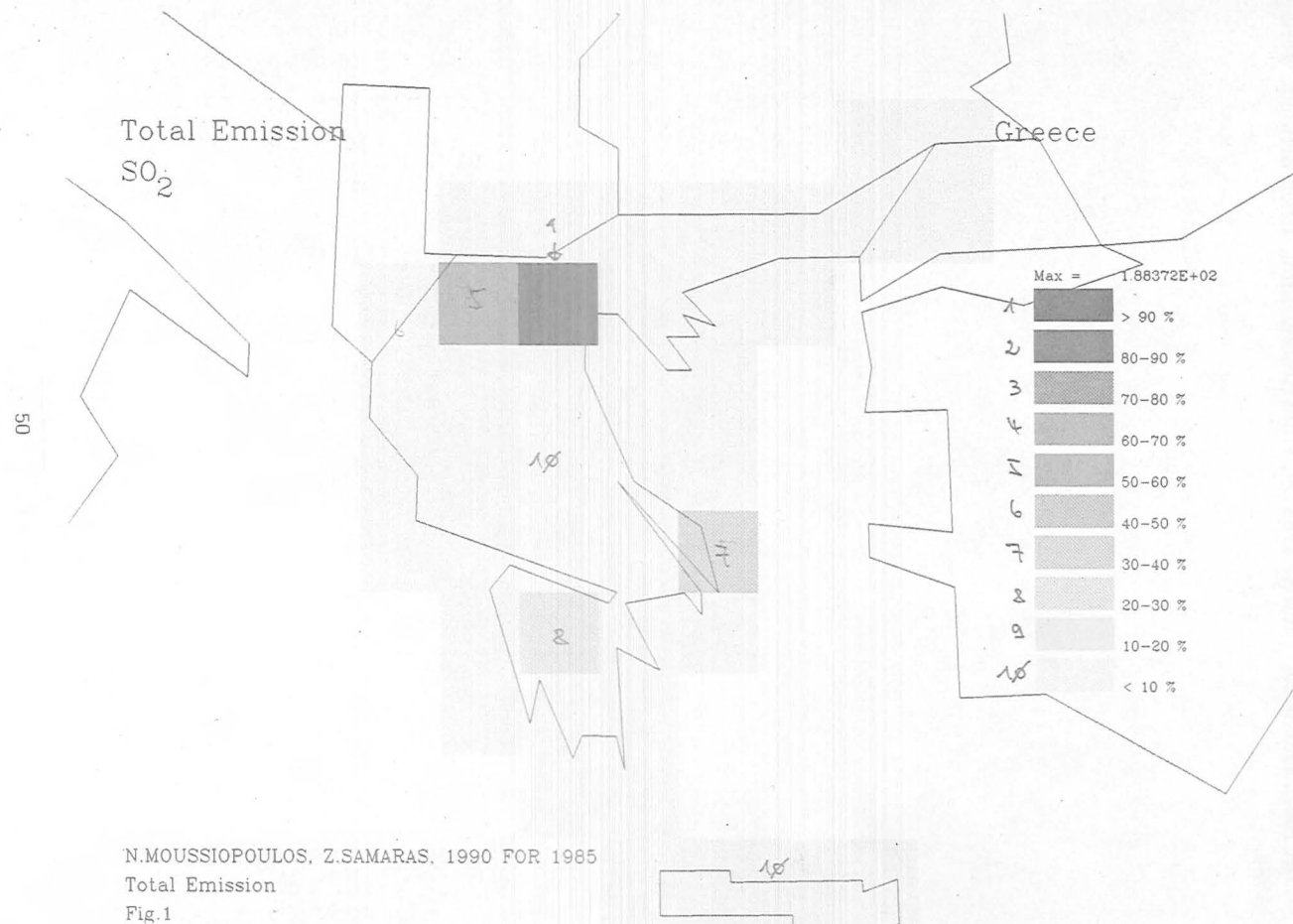
1. urban emission 147 kt/a
2. rural anthropogenic emission 175 kt/a
3. traffic emission 93 kt/a
4. power plants 1.44 kt/a
5. natural emission from forest 196 kt/a

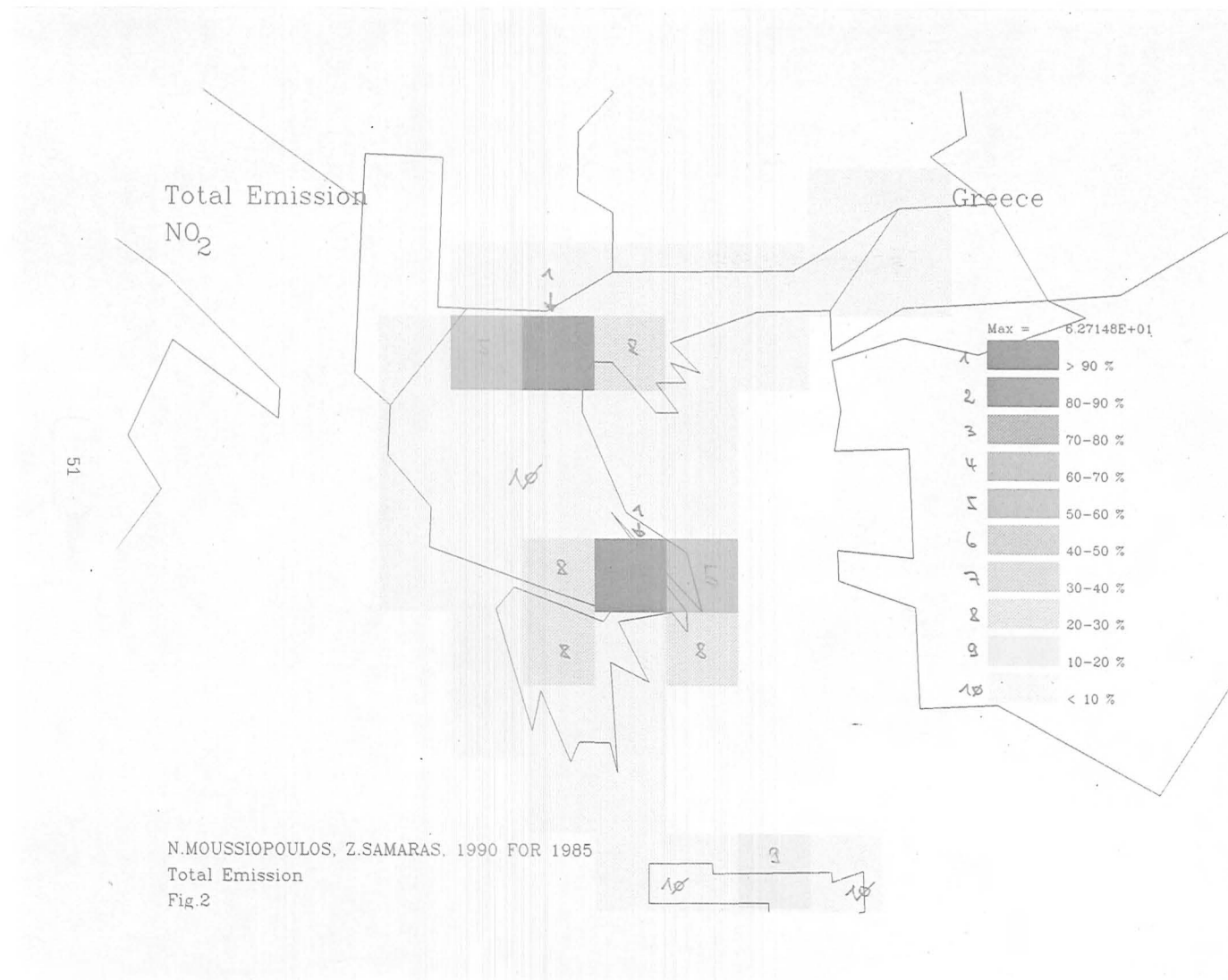
The highest contributions to urban emission according to inhabitant numbers again come from Athens (109 kt/a) and Thessaloniki (23 kt/a). The contribution to the emission from power plants is small (1.4 kt/a). The traffic emission mainly comes from Athens (41.2 kt/a) and to some extend from Thessaloniki and Kriti. Thus, the total anthropogenic VOC-emission from Athens (urban + traffic) is 150 kt/a. The natural emission from forest is concentrated in the northern part of Greece (about 20 kt/a in three grid elements north of Thessaloniki) and to some extend in Pindos and Peleponnes. The total emission is concentrated in the region of Athens due to traffic (Fig.3).

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ANTHROPOGENIC/TOTAL VOC-EMISSION FROM LUEBKERT ET AL.,1989
 N.MOSSIPOULOS, Z.SAMARAS, 1990 FOR 1985
 Total Emission
 Fig.3

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